Lipids in Proso Millet (*Panicum miliaceum*) Flours and Brans

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ABSTRACT

The lipid composition of flours and brans of nine proso millet varieties was determined. Free lipids in proso millet flours ranged from 3.20 to 4.06% and in bran from 3.45 to 6.84%. Bound lipids ranged from 0.47 to 0.89% and from 0.30 to 0.70% in flours and brans, respectively. Fatty acids were determined by gas-liquid chromatography. Linoleic acid, oleic acid, and palmitic acid were the predominant fatty acids in the free lipids of flours and brans. Free and bound lipids extracted from flours were separated by thin-layer chromatography. In the free lipids, hydrocarbons, sterol esters, triglycerides, diglycerides, and fatty acids were present. In the bound lipids, monogalactosyl diglycerides, digalactosyl diglycerides, phosphatidyl ethanolamine, phosphatidyl serine, and phosphatidyl choline were tentatively identified.

Cereal Chem. 63(5):387–390

The term "millet" is used for several small seeded annual grasses that are of minor importance in the Western world but a staple in the diets of African and Asiatic peoples. Millets can be cultivated in a wide range of soils and climates and are of special importance in semiarid regions because of their short growing seasons. Five millets are common: *Setaria italica, Pennisetum glaucum* or *P. typhoideum, Eleusine coracana, Echinochloa frumentacea,* and *Panicum miliaceum*. *Panicum miliaceum*, also known as proso millet, hershey, broom corn, or hog millet is at present the only species of economic importance in the United States (Casey and Lorenz 1977).

Proso millet is used without dehulling in livestock rations and bird seed. Suggested food applications of dehulled proso millet in the United States include a puffed or cooked breakfast cereal or replacement of wheat flour in certain baked products (Hinze 1972).

Very little research has been conducted with proso millets compared with other cereal grains. There are no reports in the literature about the lipid composition of these millets. Frequent references to the need to preserve whole grain millet and millet flours in airtight containers in order to minimize rancidity serves as a reminder of the high lipid content of some millets. Various authors report lipid contents ranging from 3.0 to 6.5% (Pruthi and Bhatia 1970; Goswami et al 1969a,b, 1970; Burton et al 1972; Freeman and Bocan 1973), which is higher than that of wheat, corn, rice, or sorghum.

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Knowledge of the lipid composition of proso millets is important to predict the storage stability of proso millet flours as well as for nutritional reasons.

MATERIALS AND METHODS

Sample Identification

This study included nine samples of proso millet, grown on summer-fallowed land at the Colorado State University Experiment Farm in Springfield, CO. The hybrids, selections, and selections from a cross of Leonard by an Akron selection are identified and described in Table I. All samples were milled in a Quadrumat Junior mill to obtain flour and a bran fraction, both of which were analyzed for lipid composition. The bran was ground in a Udy cyclone mill into a fine powder before lipid extractions.

Proximate Analyses

Millets were analyzed for moisture, crude fat, ash, nitrogen, and crude fiber by AACC approved methods 44-15A, 30-10, 08-01, 46-11, and 32-15, respectively (AACC 1976).

Lipid Extractions

Free lipids were extracted with petroleum ether for 9 hr in a Goldfish apparatus. Bound lipids were extracted three times, 1 hr each by stirring the residue with water-saturated *n*-butanol. The drying and re-extraction procedure was done as described by Daftary and Pomeranz (1965). All lipid extractions were done in duplicate.

Thin-Layer Chromatography of Free and Bound Lipids

The free and bound lipids of flours and brans were characterized by thin-layer chromatography (TLC) on 250-μm thick silica gel plates with a mixture of chloroform, methanol, and water (65:25:4, v/v) to separate polar components and with petroleum ether, diethyl ether, and acetic acid (80:20:1, v/v) to separate nonpolar components. After separation, the spots were made visible by spraying the plates with a saturated solution of $K_2Cr_2O_7$ in 55% aqueous H_2SO_4 and charring for 7 min at 150° C. Lipids were tentatively identified by cochromatography with known lipids obtained from Sigma Chemical Co.

Gas Chromatography of Fatty Acids

Aliquots of the free lipid extracts were dried under N_2 and saponified with 0.5*M* ethanolic NaOH in a 60° C water bath for 1 hr. Each sample was extracted twice with hexane. The hexane extract was discarded and the aqueous solution acidified to pH 2 with 6*N* HCl. The aqueous layer was re-extracted with hexane. The hexane layer was dried under N_2, and the residue was esterified with BF_3/methanol in a 60° C water bath for 20 min. Hexane (2 ml) was added to extract the methyl esters. This hexane extract was placed in small capped vials, frozen, and dried under N_2. Just before gas-liquid chromatography (GLC) injection, 200 μl of hexane was added to each vial, and 0.5 μl was injected into a 2-m column of 10% Silar 10C on 100/120 mesh Gas Chrom A. The operating conditions of the HP 5830A gas chromatograph were as follows: column temperature, 180° C; injection temperature, 375° C; and flame ionization detector, 300° C. Known mixtures of fatty acids (Supelco mix no. 10 and Supelco PUFA-2) were used for identification. Weight percentage compositions were calculated by applying correction factors obtained from chromatograms of the known mixture. Duplicate analyses were run on each sample.

RESULTS AND DISCUSSION

Proximate Composition and Milling Data

The proso millet samples used in this study ranged in color from creamy white to very dark brown (Table I). Compared to wheat, corn, and sorghum, the mineral content of millets is high (Lorenz et al 1976). Reported ash values for varieties of *E. coracana, P. typhoideum, S. italica,* and *P. miliaceum* range from 2.6 to 3.9% (Joseph et al 1959, Kurien 1967, Burton et al 1972). Several of the cultivars used in this study had ash contents in excess of those reported previously by others, and we have no explanation for such high ash values.

The reported range of protein in millets varies from 5.6 to 16.0% (Deosthale et al 1971, Burton et al 1972). Protein contents of millets in this study fell within the reported range. Crude fiber values of proso millets varied from 4.2 to 9.2%, which is quite high compared to other cereal grains. Such high fiber values can reduce digestibility of millets considerably (Joseph et al 1959, Deosthale et al 1971).

Milling of the proso millets in a Quadrumat Junior mill produced flour extraction rates of 79.2 to 87.1% (Table I). Lorenz et al (1980) previously used the Quadrumat Junior mill to produce a flour from proso millets with considerably lower ash and crude fiber contents compared to whole grain millets. Flour extraction rates were comparable to those obtained in this study. A reduction in ash and crude fiber is needed to make a flour or meal suitable for use in food applications.

Free and Bound Lipids of Flours and Brans

Quadrumat Junior milling of millets is reported to leave rather high levels of lipids in the flour—levels which are considerably

TABLE I
Grain Proximate Composition and Milling Data

Sample Description	Seed Coat Color	Ash[a] (%)	Nitrogen[a] (%)	Crude Fiber[a] (%)	Flour Extraction[b] (%)	Bran[b] (%)
Red proso millets						
Turghai, standard red	light brown	4.6	2.13	7.9	82.4	17.6
Akron, Colorado selection	light brown	3.0	2.36	9.2	79.2	20.8
Big Red, Russian selection	light brown	3.4	2.13	7.6	80.1	19.9
Leonard × Akron cross (LA13)	very dark brown	···	···	···	79.3	20.7
Leonard × Akron cross (LA14)	very dark brown	···	···	···	79.8	20.2
White proso millets						
Minco, white early type (Minnesota)	creamy white	3.6	2.08	4.2	82.1	17.9
Abarr, Colorado release from common white	creamy white	3.4	2.15	4.6	87.1	12.9
Leonard, Colorado release	creamy white	3.5	2.14	7.7	82.4	17.6
Dawn, Nebraska release	creamy white	7.6	2.32	6.7	85.6	14.4

[a]Determined on 14% moisture basis.
[b]All samples were milled without tempering.

TABLE II
Free and Bound Lipids of Proso Millet Flours and Brans

Sample	Flour			Bran			Grain		
	Free (%)	Bound (%)	Total[a] (%)	Free (%)	Bound (%)	Total[a] (%)	Free[a] (%)	Bound[a] (%)	Total[a] (%)
Red proso									
Turghai	3.74 ± 0.28	0.50 ± 0.07	4.24	4.29 ± 0.29	0.70 ± 0.11	4.99	3.84	0.54	4.38
Akron	4.06 ± 0.31	0.70 ± 0.11	4.76	3.45 ± 0.21	0.69 ± 0.09	4.14	3.94	0.70	4.64
Big Red	3.63 ± 0.27	0.69 ± 0.10	4.32	3.88 ± 0.34	0.36 ± 0.06	4.24	3.46	0.84	4.30
LA13	3.84 ± 0.14	0.77 ± 0.12	4.61	4.20 ± 0.41	0.30 ± 0.09	4.50	3.66	0.93	4.59
LA14	4.03 ± 0.20	0.89 ± 0.14	4.92	4.26 ± 0.39	0.38 ± 0.12	4.64	3.93	0.94	4.87
White proso									
Minco	3.72 ± 0.19	0.68 ± 0.09	4.40	6.78 ± 0.56	0.49 ± 0.15	7.27	3.61	1.30	4.91
Abarr	4.00 ± 0.26	0.47 ± 0.06	4.47	6.84 ± 0.61	0.33 ± 0.10	7.17	3.89	0.92	4.81
Leonard	3.70 ± 0.14	0.68 ± 0.14	4.38	4.32 ± 0.37	0.48 ± 0.20	4.80	3.61	0.84	4.45
Dawn	3.20 ± 0.26	0.64 ± 0.11	3.84	3.95 ± 0.30	0.39 ± 0.11	4.34	3.29	0.62	3.91

[a]Calculated; data on 14% moisture basis.

TABLE III
Fatty Acids (%) of Proso Millet Free Lipids

Fatty Acid[a]	Turghai	Akron	Big Red	LA13	LA14
Flours					
C-16:0	7.16 a	7.16 a	10.02 b	8.09 a	9.10 b
C-16:1	0.28 a	0.27 a	0.26 a	0.13 b	0.28 a
C-18:0	1.63 a	1.59 a	3.38 c	1.53 c	2.03 b
C-18:1	24.15 a	21.67 bc	21.63 bc	18.46 c	18.11 c
C-18:2	63.57 a	66.15 b	62.17 a	69.52 c	67.78 b
C-18:3	2.16 a	1.69 b	1.32 c	1.60 b	1.74 b
C-20:4	0.36 a	0.22 b	0.19 b	0.09 c	0.18 b
Brans					
C-16:0	6.30 a	6.39 a	8.56 c	5.80 b	5.67 b
C-16:1	0.30 a	0.33 a	0.34 a	0.26 a	0.23 a
C-18:0	1.49 a	1.48 a	3.06 b	1.10 a	1.09 a
C-18:1	25.27 a	22.48 a	21.69 ab	19.22 b	19.40 b
C-18:2	63.88 a	66.58 a	63.36 a	70.59 b	70.72 b
C-18:3	1.74 a	1.67 a	1.91 a	2.20 b	2.01 ab
C-20:4	0.14 a	0.35 b	0.44 b	0.34 b	0.27 b

[a] Within each fatty acid, values with different letters differ significantly ($P < 0.05$).

higher than those found in wheat flour (Lorenz et al 1980). Free lipids in proso millet flours ranged from 3.20 to 4.06% and in bran from 3.45 to 6.84%. Bound lipids in proso millet flours ranged from 0.47 to 0.89% and in bran from 0.30 to 0.70% (Table II).

The level of free lipids (petroleum-ether extractable) extracted from pearl millet cultivars varied from 3.03 to 7.40% (Ahuja et al 1979; Goswami et al 1969a,b, 1970; Lai and Varriano-Marston 1980). Bound lipid contents ranged from 0.58 to 0.90% among 18 samples of pearl millet grown in Kansas (Lai and Varriano-Marston 1980).

Fatty Acids in Free Lipids

The major fatty acids of the free lipids in flour and bran of proso millets (Table III) are linoleic acid, oleic acid, and palmitic acid. These three fatty acids represent over 90% of the fatty acids in proso millet flour and bran. Linoleic acid and oleic acid contents were slightly higher and palmitic acid content slightly lower in bran than in flour. The differences in fatty acid content between varieties was small.

Lai and Varriano-Marston (1980) reported linoleic, oleic, and palmitic acids to be the major fatty acids in free and bound lipids of pearl millet. In a study of 65 lines of pearl millet, Jellum and Powell (1971) found the following levels of fatty acids: linoleic (40.3–51.7%), oleic (20.2–30.6%), and palmitic (17.7–25.0%).

The fatty acid composition of the total lipids of wheat, barley, corn, oats, rye, sorghum, and triticale also shows linoleic acid to be the predominant fatty acid followed by oleic and palmitic acids (Price and Parsons 1975).

Lipid Composition

The major components of the free lipids of flours were triglycerides as seen in Figure 1. Minor fractions included diglycerides, sterols, free fatty acids, and sterol esters. Thin-layer chromatograms are shown for seven of the flours only, as qualitative results indicated the same number of components in all tested flours. Similar TLC separations of free lipids have been shown for pearl millet (Pruthi and Bhatia 1970, Badi et al 1976).

Free lipids in the bran fractions showed the same qualitative composition. There were no qualitative differences between the free lipids of proso millets and those of barley, corn, triticale, and wheat (Price and Parsons 1975).

A TLC separation of bound lipids of millet flours is shown in Figure 2. The bran samples showed the same qualitative bound lipid composition. Phosphatidyl-choline and digalactosyl diglycerides are the major components. Other components tentatively identified included phosphatidyl serine, phosphatidyl ethanolamine, and mono-galactosyl diglycerides. Spot intensities indicate only minor quantitative differences between flours.

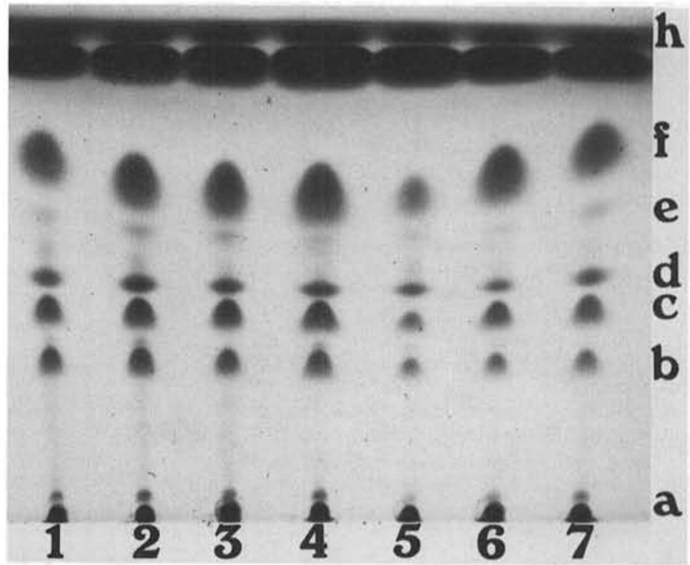

Fig. 1. Free lipids of proso millet flours: **1** = Abarr; **2** = Turghai; **3** = Leonard; **4** = Dawn; **5** = LA13; **6** = Minco; and **7** = Akron; **a** = monoglycerides and unresolved polar lipids; **b** = 1,2 diglycerides; **c** = 1,3 diglycerides; **d** = sterols; **e** = unknown; **f** = fatty acids; **g** = triglycerides; and **h** = hydrocarbons and sterol esters.

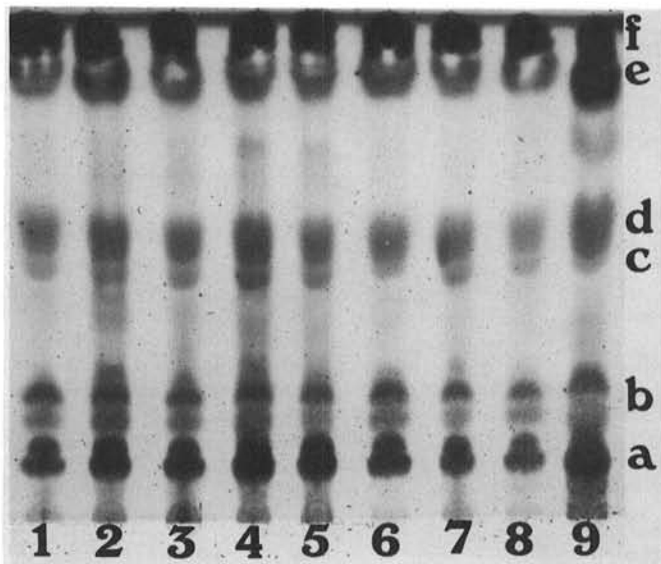

Fig. 2. Bound lipids of proso millet flours: **1** = Turghai; **2** = Akron; **3** = Big Red; **4** = LA13; **5** = LA14; **6** = Minco; **7** = Abarr; **8** = Leonard; and **9** = Dawn; **a** = phosphatidyl choline; **b** = phosphatidyl serine; **c** = phosphatidyl ethanolamine; **d** = digalactosyl diglycerides; **e** = monogalactosyl diglycerides; and **f** = unresolved nonpolar lipids.

CONCLUSIONS

The lipid composition of proso millet is quite similar qualitatively to that reported for other cereal grains. There are differences in percentage composition attributable to variety and, in flours, to differences in flour extraction rates.

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[Received November 19, 1984. Accepted April 19, 1986.]