

# Lipids of Seven Cereal Grains

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## ABSTRACT

Grain samples of representative varieties of barley, corn, oats, rye, sorghum, triticale, and wheat grown commercially in the north central US were analyzed. Chemical constituents of the varieties studied are presented to provide an overview of their characteristics.

Lipids of the milled grain samples were solvent extracted, classified by silicic acid column chromatography, and separated by thin layer chromatography. Fatty acid composition of the total lipid was determined by gas liquid chromatography and the fatty acid content was determined by saponification and extraction.

Total lipid content of the grains ranged from 2.3% for 'Polk' wheat to 6.6% for 'Chief' oats. Lipid composition varied considerably. The row crops, corn and sorghum, have a high neutral lipid and low glycolipid content. The small grain varieties have a more balanced distribution among neutral lipids, glycolipids, and phospholipids. Fatty acid composition of the total lipid was similar for all grains. Minor qualitative differences were noted among the lipid classes of the 7 cereals.

## INTRODUCTION

Lipids are an important nutritional component in feed grains. They contain 2¼ times the energy per unit wt of carbohydrates and proteins, provide essential fatty acids, add flavor factors, improve the efficiency of feed conversion, and reduce the dustiness of the milled grain.

Cultivated barley varieties have a lipid content of ca. 3% (1,2). A genetic increase in oil content in barley is highly desirable. It would improve the nutritional quality of barley and further promote its use in livestock and poultry rations. Barley competes with other feed grains for commercial use.

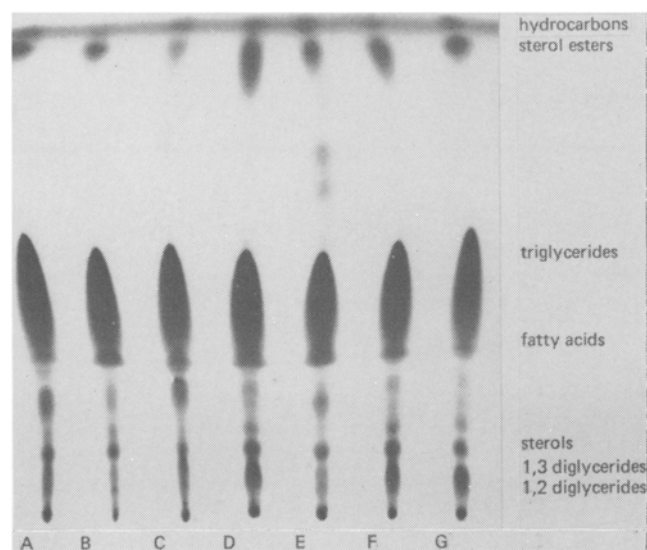


FIG. 1. Thin layer chromatographic separation of neutral lipids from 7 cereal grain varieties. Adsorbent, Silica Gel G; solvent, petroleum ether:diethyl ether:acetic acid (90:10:1); visualization, charring by heating after spraying with sulfuric acid:potassium dichromate (29). A = Prilar barley; B = Pioneer 3764-3X corn; C = Chief oats; D = Prolific rye; E = South Dakota 106 sorghum; F = North Dakota 203 Triticale; and G = Polk wheat.

More information on cereal grain lipids was needed to assess properly the competitive status of barley. This study was initiated to provide data on total lipid content, lipid composition, and the fatty acid content and composition of 7 major cereal grains.

## MATERIALS AND METHODS

Whole grain samples of 'Prilar' barley, 'Pioneer 3764-3X' corn, 'Chief' oats, 'Prolific' rye, 'South Dakota 106' sorghum, 'North Dakota 203' triticale, and 'Polk' wheat were ground in a Udy cyclone mill to pass a 0.024 in. screen. Proximate analyses of the grain were determined by AOAC procedures (3). Total lipids were extracted and purified as described previously (1,2), and separated into classes by silicic acid column chromatography. The lipids in each class were separated by thin layer chromatography (TLC) according to the techniques of Stahl (4). Typical separations are shown (Fig. 1, 2, and 3). The lipids separated by TLC were identified by comparing Rf values with authentic compounds and with published Rf values as described previously (5,6). The gas liquid chromatographic analyses including information on column and operating conditions, and the preparation of methyl esters also were described previously (1). The fatty acid content of the total lipid extract was determined by saponification (AOAC procedure (7), acidification, and extraction 3 times with petroleum ether. The petroleum ether extracts were evaporated to dryness under

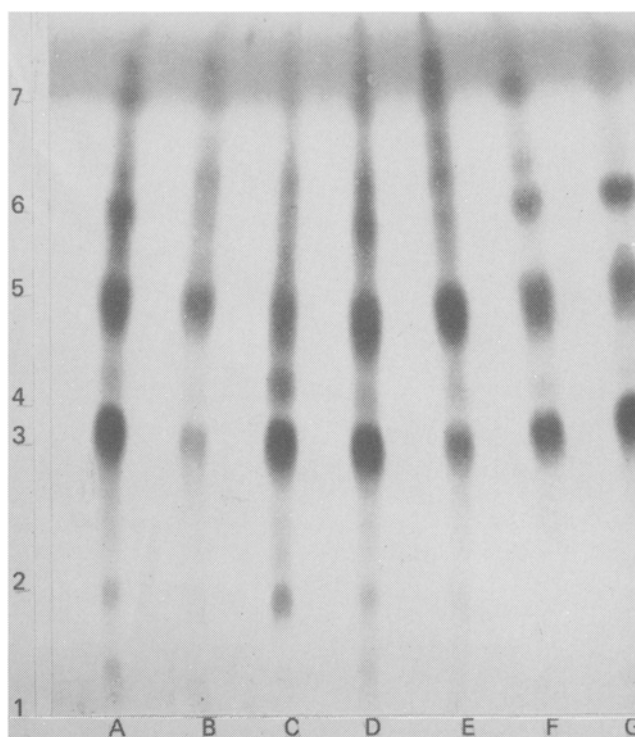


FIG. 2. Thin layer chromatographic separations of glycolipids from 7 cereal grains. Adsorbent, Silica Gel H; solvent, chloroform:methanol:water (75:25:4); visualization, charring by heating after spraying with sulfuric acid:potassium dichromate (29). A = Prilar barley; B = Pioneer 3764-3X corn; C = Chief oats; D = Prolific rye; E = South Dakota 106 sorghum; F = North Dakota 203 Triticale; G = Polk wheat. The glycolipid spots were identified as follows: 1, origin; 2, sulfatides; 3, digalactosyl diglyceride; 4, unknown; 5, unknown (sterol glycoside, cerebrosides); 6, monogalactosyl diglyceride; 7, pigments.

vacuum and weighed. The wt of each fatty acid was calculated by multiplying the wt of total fatty acids per 100 g of grain by the percent fatty acids as determined by GLC.

## RESULTS

Proximate analyses of the seven cereal grains are summarized in Table I. Probable carbohydrate content was calculated by difference after the percentages of the other chemical constituents were measured. As expected, this number of grains, "row crops" (corn and sorghum) and the "small grains" (barley, oats, rye, triticale, and wheat) showed considerable range within each food group. Lipid is the food class of primary interest here, and it ranged from 2.3% for wheat to 6.6% for oats. Protein content varied from 8.9% in corn to 19.6% in triticale, and carbohydrate reflected the accumulated differences within the other food groups. The lipid content of 'Prilar' barley, 3.2%, agreed with previously determined values (2) and with general information (1) on barley.

Total lipid composition of the seven grains is presented in Table II. Corn and sorghum had the highest neutral lipid content (91.9% and 86.2%, respectively), and they also contained the smallest quantities of glycolipids and phospholipids. The small grain varieties contained from 62 to 78% neutral lipid and higher quantities of polar lipids.

The neutral lipids from the seven cereal grains are shown in a representative TLC photo (Fig. 1). Triglycerides were the major fraction of neutral lipids. Minor fractions, including diglycerides, sterols, free fatty acids, and sterol esters, appeared to be rather constant for all grains. Sorghum showed two small spots migrating ahead of the triglycerides.

Figure 2 presents the glycolipid fractions for the cereals. Seven distinct spots developed, with no major differences among the crops. Slight differences in quantity existed, especially spot number 4 in oats.

The phospholipid fractions of these grains were remarkably similar (Fig. 3). The specific phospholipid spray of Dittmer and Lester (8) verified all the major known phospholipids, including unknowns 7 and 9. The overlapping of phosphatidyl choline, phosphatidyl serine, and phosphatidic acid was confirmed by the use of ninhydrin spray reagent, authentic standards, and two-dimensional TLC (9).

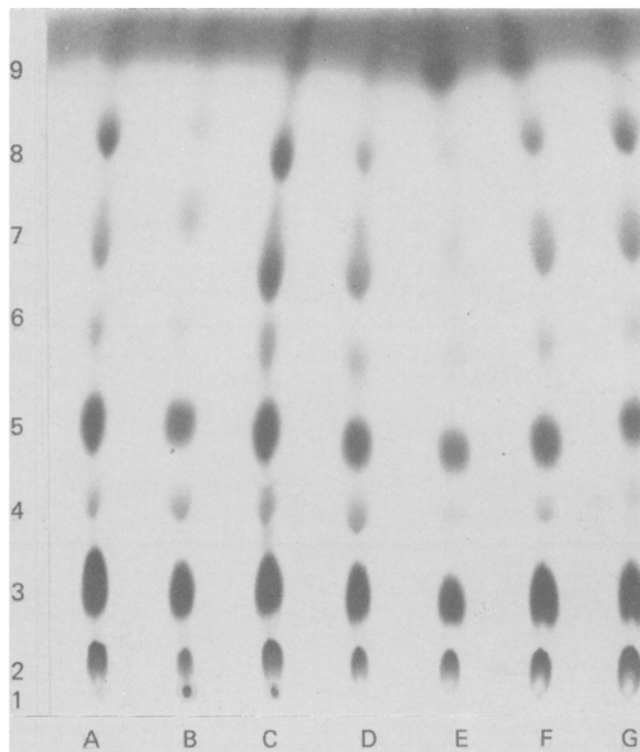


FIG. 3. Thin layer chromatographic separations of phospholipids from 7 cereal grains. Adsorbent, Silica Gel H; solvent, chloroform:methanol:water:28% aqueous ammonia (65:35:4:02); visualization, charring by heating after spraying with sulfuric acid:potassium dichromate (29). A = Prilar barley; B = Pioneer 3764-3X corn; C = Chief oats; D = Prolific rye; E = South Dakota 106 sorghum; F = North Dakota 203 Triticale; and G = Polk wheat. The spots were identified as follows: 1, origin; 2, lysophosphatidyl choline; 3, phosphatidyl choline, phosphatidyl serine, and phosphatidic acid; 4, phosphatidyl inositol; 5, phosphatidyl ethanolamine; 6, phosphatidyl glycerol; 7, unknown; 8, diphosphatidyl glycerol; and 9, solvent front.

Fatty acid composition of the total lipid extract was determined for each grain (Table III). Linoleic, oleic, palmitic, and linolenic are the major fatty acids. Smaller

TABLE I  
Proximate Analysis of Seven Cereal Grains

Grain (variety)	Ash (%)	Crude fiber (%)	Lipid (%)	Moisture (%)	Protein (%)	Probable carbohydrate (by difference) (%)
Barley ('Prilar')	2.9	4.1	3.2	8.9	12.5	68.4
Corn ('P3764-3X')	1.3	3.1	5.8	8.3	8.9	72.6
Oats ('Chief')	3.7	11.3	6.6	8.4	16.6	53.4
Rye ('Prolific')	2.2	1.5	3.6	10.1	18.9	63.7
Sorghum ('South Dakota 106')	2.0	2.8	3.3	9.2	11.9	70.8
Triticale ('North Dakota 203')	2.5	2.6	2.4	9.2	19.6	63.7
Wheat ('Polk')	2.2	2.0	2.3	9.6	18.1	65.8

TABLE II  
Lipid Composition of Seven Cereal Grains

Grain (variety)	Composition (%)		
	Neutral lipid	Glycolipid	Phospholipid
Barley ('Prilar')	78.2	7.3	14.5
Corn ('P3764-3X')	91.9	2.1	6.0
Oats ('Chief')	72.9	17.0	10.1
Rye ('Prolific')	71.0	10.7	18.3
Sorghum ('South Dakota 106')	86.2	3.1	10.7
Triticale ('North Dakota 203')	66.9	16.0	17.1
Wheat ('Polk')	61.9	21.6	16.5

TABLE III  
Fatty Acid Composition of Total Lipids of Seven Cereal Grains<sup>a</sup>

Grain (variety)	Fatty acid (% by wt)						
	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3
Barley ('Prilar')	0.45	20.82	0.18	1.01	17.82	55.31	4.41
Corn ('P3764-3X')	0.44	13.37	0.15	1.93	23.99	59.29	0.83
Oats ('Chief')	0.66	18.04	0.11	1.24	36.34	42.02	1.59
Rye ('Prolific')	0.30	14.98	0.37	0.83	19.15	57.62	6.75
Sorghum ('South Dakota 106')	0.20	19.48	0.80	1.70	28.13	44.73	4.96
Triticale ('North Dakota 203')	0.14	16.57	0.24	0.62	13.66	63.78	4.99
Wheat ('Polk')	0.19	17.16	0.33	1.44	20.38	57.66	2.84

<sup>a</sup>Percent by wt calculated from peak areas of the gas chromatograms, Fatty acids are expressed as number of carbons: number of double bonds.

TABLE IV  
Fatty Acid Content of Seven Cereal Grains

Grain (variety)	Fatty acid (%)	Wt fatty acid (mg/100g grain)	Wt of fatty acids (mg/100 g grain)						
			C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3
Barley ('Prilar')	74.5	2384	10.7	496.4	4.3	24.0	424.8	1318.7	105.1
Corn ('P3764-3X')	90.8	5268	23.2	704.3	7.9	101.7	1263.8	3123.4	43.7
Oats ('Chief')	66.9	4415	29.1	796.5	4.9	54.7	1604.4	1855.2	70.2
Rye ('Prolific')	84.2	3031	9.1	454.0	11.2	25.2	580.4	1746.5	204.6
Sorghum ('South Dakota 106')	76.7	2532	5.1	493.2	20.3	43.0	712.3	1132.6	125.6
Triticale ('North Dakota 203')	81.6	1957	2.7	324.3	4.7	12.1	267.3	1248.2	97.7
Wheat ('Polk')	75.3	1731	3.3	297.0	5.7	24.9	352.8	998.1	49.2

<sup>a</sup>Determined by saponification and wt of free fatty acids.

quantities of stearic, myristic, and palmitoleic also were detected. Linoleic is the predominant unsaturated fatty acid, present in amounts of 55-64% of the total for all but oats and sorghum. These two were higher in oleic (36% and 28%), and had linoleic yields of 42% and 45%, respectively. Linolenic acid was found at levels of 3-7% in 5 grains, but was somewhat lower for corn (0.83%) and oats (1.59%).

The fatty acid content of the total lipid extract was determined for each grain (Table IV). The percent fatty acids in the total lipid ranged from a low of 67% for oats to a high of 91% for corn. Saponification and extraction procedures provided the conversion factors needed to calculate the yield of each fatty acid in mg/100 g of grain.

## DISCUSSION

The data on proximate analyses (Table I) are included here to provide an overview of the nutritional components of the major cereals. The chemical composition of these grains is comparable to that published by the National Academy of Sciences (10). The variability which exists among these cereals (Table I) within each food class illustrates the complementary effect of each class on total nutritional content. Barley compares favorably with the other grains except for its lipid content, which is considerably lower than that of corn and oats.

Previous studies on cereal grain lipids have been reported for barley (1,2,11-13), corn (14-16), wheat (17-21), oats (22), rye (22), sorghum (23), and for plants in general (24). A review of cereal lipids, content, composition, and potential industrial use by Weber (25) provides additional information on lipid analyses. Comparisons between results of this study and some of those cited are difficult because of differences in extraction procedures and solvents. Petroleum ether was the extractant used for barley (11-13), wheat (17,19), and sorghum (23). Petroleum ether and ethanol were used for oats and rye (22). Petroleum ether and ethanol extract neutral lipids, but are unsatisfactory for removing the polar lipids, glycolipids, and phospholipids. When other investigators used the same solvent system, chloroform:methanol:water, comparable results were ob-

tained. Weber (14,15) found that mature corn had 92% neutral lipid and 8% polar lipid. We obtained almost identical results (Table II). Lin, et al., (21) reported distribution of the total lipid of the spring wheat variety 'Selkirk' to be 51.3% neutral lipid, 22.8% glycolipid, 19.4% phospholipid, and 6.5% unresolved lipid. A similar distribution was obtained with the spring wheat varieties 'Chris' and 'Red River 68.' The total lipid distribution in this study (Table II) for the spring wheat variety 'Polk' was 61.9% neutral lipid, 21.6% glycolipid, and 16.5% phospholipid.

Of the two migrating spots found for sorghum in Fig. 1, smaller amounts of the upper spot also were noted for barley and oats (not visible in Fig. 1), so only the lower spot appeared to be an exclusive fraction of this grain. These spots have not been identified, but they may be esters.

Of the glycolipids (Fig. 2), two major spots, monogalactosyl diglyceride and digalactosyl diglyceride, are well defined. A third major spot, less well defined, compares with authentic standards as sterol glycoside and cerebrosides. Allen and Good (24) reported that these compounds are universal constituents of photosynthetic tissue. As shown here, they are present in relative abundance in storage tissues as well.

Phosphatidyl choline, phosphatidyl ethanolamine, and lysophosphatidyl choline are the most abundant phospholipids of cereal grains (Fig. 3). Phospholipids have a role in membrane development, fatty acid, and phytin synthesis (14). The role of glycolipids and phospholipids in seed development and seed viability is only partially known.

The fatty acids present in the total lipid of the seven grains were typical for most seeds (Table III). Linoleic acid was the major fatty acid present, although oats and sorghum were lower. Our data agree with those of Aylward (22), who reported on barley and oats, and with Edwards (26), who reported on barley, corn, milo, oats, and wheat.

Total lipid content is a major consideration in evaluating the energy content of a cereal grain. The fatty acid content of the total lipid is equally important. Kinsella (27) has emphasized the need for a determination of the fatty acid content of the total lipid extract. Our data (Table IV) reveal the superiority of corn in percent of fatty acid, wt of

total fatty acid, and wt of the essential fatty acid, linoleic. The top position of corn in these categories undoubtedly contributes to its popularity as a nutritious, high energy feed.

Barley is relatively low in total lipid content. Consequently, it is low in the amount of fatty acids present, including the essential fatty acids, linoleic and linolenic. The results of this study clearly demonstrate the need for genetic improvement in barley lipids. However, genetic changes will have to be carefully evaluated, in view of the fatty liver-hemorrhagic syndrome in chickens, which has become a problem in recent years (28). Over-consumption of lipid energy and/or the lack of dietary lipotropic substances are probable causes of this disease.

This study provides a comparison of the lipids of the major cereal grains extracted with proven techniques. We have presented this information because it is useful to the food industry and nutritionists in formulating diets for humans and grain rations for livestock.

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