TABLE I

Yields and Lipide Contents of Bran Fractions and True Pericarp and Germ Fractions (Moisture-Free Basis)

Variety	Stuttgart, Arkansas				Crowley, Louisiana				Beaumont, Texas			
	Bran		True Pericarp and Germ		Bran		True Pericarp and Germ		Bran		True Pericarp and Germ	
	Amount m.f.b.	Lipide Content m.f.b.	Amount m.f.b.	Lipide Content m.f.b.	Amount m.f.b.	Lipide Content m.f.b.	Amount m.f.b.	Lipide Content m.f.b.	Amount m.f.b.	Lipide Content m.f.b.	Amount m.f.b.	Lipide Content m.f.b.
	%	%	%	%	%	%	%	%	%	%	%	%
Magnolia	6.4	21.0	5.9	22.7	5.4	21.2	4.9	23.2	6.1	22.2	5.8	23.4
Bluebonnet	4.0	20.1	3.4	23.8	6.0	17.4	5.1	20.3	5.0	22.2	4.5	24.6
Blue Rose	5.0	23.0	4.8	23.9	5.8	20.9	5.3	22.8	6.7	19.3	6.1	21.3
Zenith	5.4	19.7	4.8	22.1	6.5	20.2	5.7	23.1	6.8	20.4	6.1	22.6
Caloro	5.4	21.2	5.1	22.6	6.4	20.2	5.8	22.4	6.2	18.0	5.5	20.2
Fortuna	5.1	16.0	4.1	19.6	6.4	18.5	5.3	22.1	5.6	20.6	5.1	22.7
Early Prolific	6.2	19.3	5.7	20.8	7.1	16.9	5.9	20.1	6.3	19.7	5.7	21.5
Prelude	7.5	15.3	6.2	18.5	7.0	16.1	6.1	18.4	6.8	18.7	6.2	20.4
Average	5.6	19.5	5.0	21.8	6.3	18.9	5.5	21.6	6.2	20.1	5.6	22.1

Summary

The examination of rough rice of eight varieties grown in three locations each showed variations in milling yields and lipide contents of bran and of the true pericarp and bran fraction which are attributable to the influence of variety and environment of growth. The average values found on the moisture-free basis were 6.0% bran and 5.4% true pericarp and germ fraction for the rough rice and 19.5 and 21.8% lipides in the bran and the true pericarp and germ fraction, respectively.

Acknowledgment

The authors wish to express their appreciation to C. R. Adair, N. E. Jodon, and H. M. Beachell of the Bureau of Plant Industry, Soils, and Agricultural Engineering for the rough rice samples; to W. D. Smith of the Grain Branch of the Production and Marketing Administration for use of rice milling equipment; and to Claire Lesslie for the lipide determinations.

REFERENCES

1. American Oil Chemists' Society, Official and Tentative Methods. Second ed. Edited by V. C. Mehlenbacher, Chicago, 1946. Method Aa 4-38.
2. Association of Official Agricultural Chemists, Official and Tentative Methods of Analysis. Sixth ed. The Society, Washington, 1945. Method 20.47.
3. Brown, C. A., Jr., J. Am. Chem. Soc., *25*, 948 (1903).
4. Cruz, A. O., and West, A. P., Philippine J. of Science, *47*, 487 (1932).
5. Hoffpauir, C. L., J. Assoc. Off. Agri. Chem., *32*, 291 (1949).
6. Reddi, P. B. V., Murti, K. S., and Feuge, R. O., J. Am. Oil Chem. Soc., *25*, 206 (1948).
7. U. S. Agricultural Marketing Service, Service and Regulatory Announcement No. 147, Rev. 1941.
8. U. S. Bureau of Agricultural Economics, Handbook of Official Standards of Milled Rice, Brown Rice, and Rough Rice. Prepared by E. G. Boerner, Form 179, January 1928.
9. Yampolsky, Cecil, Wallerstein Laboratories Communications, *7*, 7 (1944).

[Received June 27, 1950]

Fatty Acid Compositions of Lipids From Corn and Grain Sorghum Kernels

A. R. BALDWIN and M. S. SNIEGOWSKI, George M. Moffett Research Laboratories, Corn Products Refining Company, Argo, Illinois

OIL from corn germ has been the subject of several fatty acid composition studies (1, 2, 3, 4) and one investigation of glyceride composition (5). Analyses (6, 7, 8, 9) of the fatty acids associated with corn starch have indicated a much higher percentage of saturated acids than are present in germ oil. However no comparison of the lipids from all portions of the corn kernel has been made. The present study includes fatty acid analyses of the lipids associated with the four main fractions (germ, starchy endosperm, horny endosperm or gluten, and fiber which is mainly cell walls and epidermal tissue) obtained in the wet milling of commercial yellow hybrid corn.

Grain sorghum is assuming an ever-increasing role in the grain processing industry. Plants are in operation for both the dry and wet milling of the grain, and oil is being produced in tank car quantities. Analyses reported (4, 10) for the fatty acid composition of the germ oil indicate that it is similar to corn germ oil. A starch fat analysis has been reported recently (9). The grain contains a wax coating which is mainly absent from corn kernels (4). The present report also describes lipids obtainable from the wet milling of grain sorghum and compares them with the corresponding materials from the processing of corn.

Isolation and Preparation of Lipid Samples

A brief description of the essential features of the wet milling industry is necessary in order to provide a more complete picture of the type and source of samples used in this study. Grain, after removal of foreign materials, is steeped in dilute aqueous sulfur dioxide solution (approx. 0.2%) for about 48 hours at 130°F. This steeping operation removes most of the water solubles, such as sugars, some proteins, and minerals. The grain is then roughly ground in a Foos mill to liberate the germ which is separated by flotation. After washing, the germ is dried and the oil is recovered by expelling and/or solvent extraction. The samples used for analyses were crude expelled oils.

The non-germ portion of the grain is reground in buhrstone mills, and "fiber" is separated by screening. This "coarse fiber," which consists of hull materials with adhering endosperm, is washed and dried for feed. The sample of corn coarse fiber used for these tests was washed thoroughly to remove starch and gluten, dried, and extracted with hexane and carbon tetrachloride in the laboratory for recovery of fat. Kummerow (4) has reported on the waxy constituents of the hull of grain sorghum. After a coarse screening the starch-gluten slurry is ordinarily passed through silk or nylon shakers to remove the "fine fiber" which represents primarily the inner cell tissue materials of the grain. For these analyses the fine fiber was prepared in the same manner as the coarse fiber.

Starch-gluten slurry which contains about 90% starch and 10% gluten is then allowed to flow slowly over long, narrow, inclined tables. Starch settles onto the table as a hard cake, and the gluten passes with most of the water to settling tanks. The separated starch is then washed, filtered, and either dried for dry starch applications or sent in slurry form to the converters for the manufacture of dextrose and syrups. Starch contains approximately 0.6% of fat which is liberated during the hydrolysis. It, along with small amounts of protein, is skimmed or filtered from the crude sugar or syrup solutions and dried with the other feed constituents. Samples of this starch fat were obtained before drying of the "refinery mud" as these skimmings are called. The fat was extracted from the wet slurry with methanol, hexane, and carbon tetrachloride.

Gluten from the settling tanks is filtered to remove water and dried in rotary driers for feed. Fat associated with it can be obtained by extraction with the common fat solvents. Commercially this fat is obtained as a by-product in the manufacture of the corn protein, zein, through the following process: gluten is extracted with an aqueous alcohol to remove zein and fat from the residue gluten which is returned to the feed channel. The zein-fat solution is in turn extracted with hexane to remove the oil which is called "xanthophyll" oil. Zein is recovered from the alcohol and dried. The gluten oils from both corn and grain sorghum used in the present analyses were obtained by hexane and carbon tetrachloride extraction of dry gluten in the laboratory.

A simplified flow sheet for the wet milling of both corn and grain sorghum is shown in Figure 1.

Analytical Methods and Data

Desolventized and dried fats were first characterized as shown in Table I by determination of free fatty acids (A. O. C. S.), saponification equivalent, iodine value (Wijs, 1/2 hour) and unsaponifiable matter (modified Kerr-Sorber).

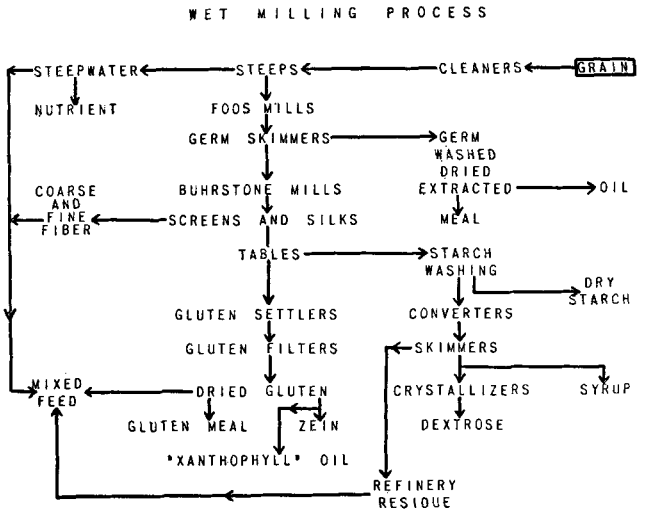


FIG. 1. Flow sheet indicating source of lipid samples from the wet milling process.

TABLE I

Characteristics of Corn and Grain Sorghum Lipids

Source of Fat	Amount of fat	Free fatty acid	Saponification equivalent	Iodine value	Unsaponifiable matter
	% d. b.	% as oleic			%
Corn germ	56.8	2.5	294	126	2.9
Grain sorghum germ	52.1	2.0	294	122	1.7
Corn starch	0.6	71.5	284	103	3.2
Grain sorghum starch	0.9	91.3	280	94	2.5
Corn gluten	7.0	22.2	324	129	13.6
Grain sorghum gluten	6.9	21.7	309	98	8.0
Corn "fine fiber"	1.3	13.8	366	108	22.8
Grain sorghum "fine fiber"	3.2	19.9	320	113	10.4
Corn "coarse fiber"	1.0	16.6	395	96	32.3

Since the supplies of fats from the fiber fractions were insufficient for a methyl ester fractionation study, the fatty acid analyses of the fiber fats were made on the liberated fatty acids after saponification of the fats. The method used was essentially the spectrophotometric method of the Spectroscopy Committee of the American Oil Chemists Society (11). Compositions obtained are given in Table II.

Fatty acid analyses of all the other fats were made by utilizing the methyl ester fractional distillation technique and spectrophotometric analysis for polyunsaturated constituents. Details of only one analysis (corn germ oil) will be given for exemplary purposes.

Approximately 150 g. of oil was saponified by heating in an alcoholic solution of potassium hydroxide. The resulting soaps were diluted to 50% aqueous alcohol and acidified with dilute sulfuric acid. The liberated fatty acids were extracted with ethyl ether and washed free of inorganic impurities. After desiccation with anhydrous sodium sulfate and removal

TABLE II

Fatty Acid Compositions of Lipids From Corn and Grain Sorghum Fibers

Fiber	Non-conjugated acids				Conjugated acids		
	Dienoic	Trienoic	Mono-unsaturated	Saturated[a]	Dienoic	Trienoic	Tetraenoic
	%		%	%	%	%	%
Corn fine	41.4	0.7	41.1	13.1	3.1	0.3	0.3
Grain sorghum fine	38.8	0.0	44.5	14.3	1.8	0.5	0.1
Corn coarse	30.6	2.1	43.2	20.0	3.5	0.3	0.3

[a] Acid equivalents of grain sorghum fine fiber and corn coarse fiber fats indicated that acid chain lengths are primarily C_{16} and C_{18}. That for corn fine fiber acids indicated considerable amounts of high molecular weight acids.

TABLE III

Distilled Corn Germ Oil Methyl Ester Fractions

Fraction	Refractive index (45°C.)	Iodine value	Saponification equivalent	Weight	Saturated				Mono-unsaturated		Di-unsaturated
					C_{14}	C_{16}	C_{18}	C_{20-22}	C_{16}	C_{18}	C_{18}
				g.	g.	g.	g.	g.	g.	g.	g.
1	1.4315	5.5	265.4	1.79	0.34	1.36	.....	.....	0.06	0.01	0.02
2	1.4317	8.3	271.8	3.51	.....	3.29	.....	.....	0.06	0.05	0.11
3	1.4369	52.2	277.3	5.28	.....	3.57	.....	.....	.....	0.22	1.49
4	1.4409	82.1	282.0	3.96	.....	1.76	.....	.....	.....	0.63	1.57
5	1.4421	94.0	284.6	11.29	.....	4.02	.....	.....	.....	2.22	5.05
6	1.4455	120.6	291.6	13.64	.....	1.85	0.17	.....	.....	4.14	7.48
7	1.4477	138.2	295.3	19.43	.....	.....	0.70	.....	.....	6.27	12.46
8	1.4479	137.4	295.3	89.52	.....	.....	3.70	.....	.....	28.78	57.04
Residue	.....	98.0	303.0	2.44	.....	.....	0.15	0.39	.....	1.02	0.88
Total as esters				150.86	0.34	15.85	4.72	0.39	0.12	43.34	86.10
Total as acids				143.64	0.32	15.04	4.50	0.37	0.11	41.30	82.00
% by wt. as acids				100.0	0.2	10.5	3.1	0.2	0.1	28.8	57.1

of solvent, the acids were esterified by refluxing with anhydrous methanol containing 1% sulfuric acid for at least 4 hours. The mixture was concentrated by distillation, and ethyl ether was added. Mineral acid was removed by water washing. Small amounts of free fatty acids were removed by washing the ether solution with a mixture of saturated sodium bicarbonate and 5% potassium carbonate. Residual alkali and soaps were finally washed out with distilled water. The other solution was dried with anhydrous sodium sulfate and the solvent removed *in vacuo*.

The methyl esters were distilled in a fractionating column 70 cm. long and 2.5 cm. inside diameter packed with single turn glass helices (12) with a calculated efficiency of about 17 theoretical plates (13). A 250-ml. flask having a thermometer well and heated with a "Glas-Col" heating mantle was used as the still pot. A total condensation, partial take-off, distilling head was used to collect the fractions (14) at a head pressure of 1-1.5 mm. of mercury.

Collected fractions were weighed and analyzed for refractive indices, Wijs (1/2 hour) iodine values, saponification equivalents, and linoleic acid contents by a modification(15) of the spectrophotometric method (16) for the determination of dienoic and polyunsaturated acids. Fatty acid composition of each fraction was calculated using equations described previously (17). Compositions of each fraction and the complete fatty acid composition of corn oil are shown in Table III.

The other corn and grain sorghum kernel fats were analyzed in the same manner and results are shown in Table IV.

TABLE IV

Fatty Acid Compositions of the Lipids From Various Parts of the Corn and Grain Sorghum Kernels

Fatty acid	Germ		Starch		Gluten	
	Corn [a]	Grain Sorghum	Corn [a]	Grain Sorghum	Corn	Grain Sorghum
Myristic,%	0.2	0.6	0.7	0.4	0.6	2.2
Palmitic,%	9.9	10.2	26.3	31.6	11.4	14.0
Stearic,%	2.9	4.1	2.8	5.4	3.5	6.0
C_{20-22},% (saturated)	0.2	trace	1.5	0.1	0.2	trace
Hexadecenoic,%	0.5	0.4	0.8	0.6	0.3	0.5
Oleic,%	30.1	32.2	20.7	22.0	28.1	29.6
Linoleic,%	56.2	51.5	47.2	39.9	53.3	45.4
Polyunsaturated,% (as linolenic)	0.0	1.0	0.0	0.0	2.6	2.3

[a] Average analyses on two different samples.

Discussion

Consideration of the characteristics (Table I) of the corn and grain sorghum lipid materials shows that a) germ oil is primarily a mixture of triglycerides, b) gluten and fiber fats contain large amounts of free fatty acids, and c) starch fat is predominantly free fatty acid.

Unsaponifiable matter of gluten and fiber fat is very high as compared to that of the germ and starch lipids. Starch fats are least unsaturated.

It is evident from the data in Tables II and IV that variations in fatty acid composition among the corn kernel fats are similar to the variations shown by the grain sorghum fats except that the grain sorghum fats are more saturated. Generally, the following considerations hold for the fats of both grains: a) starch fats contain less oleic and linoleic acids with a correspondingly higher amount of saturated acids, primarily palmitic, than is the case with either the germ, gluten, or fiber lipids; b) gluten and germ fats have approximately similar amounts of oleic and linoleic acids with the gluten fats showing an additional amount of "polyunsaturated" acidic material possibly formed by oxidation or polymerization during drying of the gluten; c) fiber fats, somewhat similar in fatty acid composition to the gluten and germ fats, also show small amounts of polyunsaturated material, along with some nonconjugated material (however, the latter was not found in the fat from grain sorghum fine fiber); and d) all the lipids examined contain predominantly palmitic, oleic, and linoleic acids, with myristic, stearic, hexadecenoic, saturated "C_{20-22}," and "polyunsaturated" acids appearing in very minor quantities.

The polyunsaturated material appearing in comparatively substantial quantities in the fiber and gluten fats, and in trace quantities in the other fats may be due to autoxidation (18, 19) occurring during grain storage and/or processing of the various fractions, or may be due to the type of interfering substances noted by Potter and Kummerow (20). Considerable care, such as use of nitrogen blankets over reaction mixtures and distillation at low temperatures under vacuum, was exercised in the laboratory to prevent oxidation.

Summary

Characteristics and fatty acid compositions of the lipid components of the main fractions (germ, starch, gluten, and fiber) obtained in the wet milling of corn and grain sorghum kernels have been determined.

The various lipids exhibited differences in chemical characteristics and fatty acid composition. These

differences were found to be similar in both grains. Germ fats were the most unsaturated, contained the least free fatty acids and the least unsaponifiable matter. Starch fats were 70 to 90% free fatty acids and contained large amounts of palmitic acid. Gluten and fiber fats contained up to 32% unsaponifiables and about 20% free fatty acids.

REFERENCES

1. Baughman, W. F., and Jamieson, G. S., J. Am. Chem. Soc., *43*, 2696-2702 (1921).
2. Longenecker, H. E., J. Biol. Chem., *129*, 13-22 (1939).
3. Baur, F. J., Jr., and Brown, J. B., J. Am. Chem. Soc., *67*, 1899-1900 (1945).
4. Kummerow, F. A., Oil and Soap, *23*, 167-70 (1946).
5. Doerschuk, A. P., and Daubert, B. F., J. Am. Oil Chem. Soc., *25*, 425-33 (1948).
6. Taylor, T. C., and Lehrman, Leo, J. Am. Chem. Soc., *48*, 1739-43 (1926).
7. Evans, J. W., and Briggs, D. R., Cereal Chem., *18*, 443-61 (1941).
8. Evans, J. W., and Briggs, D. R., Cereal Chem., *18*, 465-8 (1941).
9. Sniegowski, M. S., and Baldwin, A. R., Die Stärke, in press.
10. Kummerow, F. A., Oil and Soap, *23*, 273-5 (1946).
11. Report of the Spectroscopy Committee, J. Am. Oil Chem. Soc., *26*, 399-404 (1949).
12. Longenecker, H. E., J. Soc. Chem. Ind., *56*, 199T-202T (1937).
13. Norris, F. A., and Terry, D. E., Oil and Soap, *22*, 41-6 (1945).
14. Baldwin, A. R., and Longenecker, H. E., J. Biol. Chem., *154*, 255-65 (1944).
15. Baldwin, A. R., and Longenecker, H. E., Oil and Soap, *22*, 151-3 (1945).
16. Mitchell, J. H., Jr., Kraybill, H. R., and Zscheile, F. P., Ind. Eng. Chem., Anal. Ed., *15*, 1-3 (1943).
17. Longenecker, H. E., Oil and Soap, *17*, 53-7 (1940).
18. Hilditch, T. P., and Shrivastava, R. K., Analyst, *72*, 527-31 (1947).
19. Swain, M. L., and Brice, B. A., J. Am. Oil Chem. Soc., *26*, 272-7 (1949).
20. Potter, G. C., and Kummerow, F. A., J. Am. Oil Chem. Soc. *27*, 190-2 (1950).

[Received June 19, 1950]

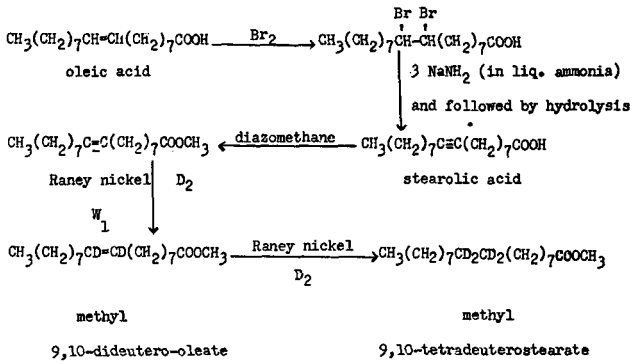
The Preparation of Stearolic Acid and Methyl Dideutero-Oleate, and Certain of Their Derivatives[1,2]

N. A. KHAN,[3] F. E. DEATHERAGE, and J. B. BROWN, Departments of Physiological Chemistry and Agricultural Biochemistry, Ohio State University, Columbus, Ohio

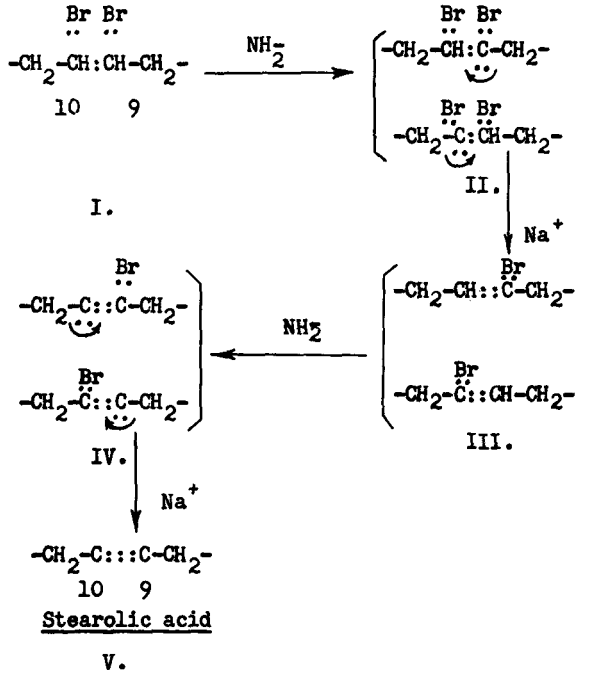
IN connection with proposed studies on the mechanism of the autoxidation of methyl oleate it was desired to prepare methyl dideutero-oleate (methyl 9,10-dideutero-cis-9-octadecenoate). This compound was synthesized by the selective reduction of methyl stearolate with deuterium, using W_1 Raney nickel (1). By fractional crystallization at low temperature (2,3) the 9,10-dideutero-oleate was separated from the unreacted stearolate and the complete reduction product, methyl tetradeuterostearate.

Earlier methods (5-8) and the more recent one published in "Organic Syntheses" (4), in which alcoholic potassium hydroxide was used for the dehydrohalogenation of 9,10-dibromostearic acid and its esters, gave relatively low yields of stearolic acid. However by reaction of sodamide on dibromostearic acid in liquid ammonia, 58-68% yields were readily obtained. Further, dehydrobromination of methyl dibromostearate by this procedure gave the amide of stearolic acid which was hydrolyzed to stearolic acid in relatively better yield and purity.

The over-all scheme of methyl dideutero-oleate synthesis is as follows:



Examination of the ozonization and peracid decomposition products of stearolic acid, thus prepared, showed no evidence of simultaneous formation of allenic and 8- and 10-octadecynoic acids (9). This fact, together with the observed nature of the freezing point curve and the homogeneity of the fractions of methyl stearolate, obtained by fractional distillation, are indicative of its purity. The mechanism of the dehydrobromination may, therefore, be outlined as follows:



The dehydrobromination appears to be completed in two stages, I-III and III-V, each involving 1,2-elimination of a mole of hydrogen bromide, and leaves no room for shifting of triple bond to give isomers.

9,10-Diketostearic acid was obtained in 90% yield by neutral permanganate oxidation of stearolic acid. [Yields of less than 27% have been previously reported (10-11)]. We have also prepared diketostearic acid directly from the oleic acid in 40% yield

[1] Submitted to the Graduate School, Ohio State University, in partial fulfillment of the requirements for the Ph.D. degree.
[2] Supported in part by grants-in-aid from the Graduate School and the Institute of Nutrition and Food Technology.
[3] Scholar of the government of Pakistan.