processing. Loder (*U. S. 2,388,164*) prepared glycerol ether esters, such as mono- and dimethoxy acetates of glycerol β-methyl ether, for use as intermediates for the manufacture of glycolates.

Several improvements in the manufacture of glycerol by the fermentation process were patented. Fulmer *et al.* (*U. S. 2,388,840*) carried out the fermentation in the presence of sulfite salts. Hodge (*U. S. 2,381,052*) promoted glycerol formation by adding ammonia to the fermentation mash in order to maintain an ammonia content of 0.1-1.0%. Hoyt (*U. S. 2,381,055*) designed a scheme for purification of a 25% glycerol concentrate from distillery slop. Some of the steps involved were digestion with sulfuric acid, treatment with lime paste, precipitation, treatment with adsorbents, and distillation. According to the method of Walmesley (*U. S. 2,389,173*) for recovering glycerol, the fermented liquors were evaporated to about 40% water content, alkaline earth material was added, and the mixture was extracted with alcohol. Wallerstein and Alba (*U. S. 2,366,990*) recovered pure glycerol from fermented carbohydrate solutions by adding formaldehyde, and maintaining the solution alkaline for one hour and then fractionally distilling.

The Composition of Sorghum Grain Oil[1] Andropogon Sorghum var. vulgaris

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STUDIES which involved characterization of the starch in sorghum grain at this station[3] (1) created an interest in the lipid material as well. Sorghum grain is now being processed for starch on a commercial scale, but no oil is being extracted in this operation[4] (2). The volume of sorghum grain produced, which for 1944 was approximately 181,500,000 bushels[5] (3), offers an opportunity for the development of a new source of oil as well as of starch. It therefore seemed desirable to compare the composition of sorghum grain oil with a commercially available oil such as corn oil.

Various analyses for the lipid material in sorghum grain have been reported (1,4,5,6). It was found that in contrast to the clear oil obtained from corn on extraction with ethyl ether, the extract of sorghum grain was a semisolid translucent material. Francis and Friedemann attempted to separate this semisolid material by centrifugation (7). Their characterization of the liquid and sediment fractions indicated that these fractions differed in melting point but not in composition. Yamamoto and Ninomiya (8) believed the liquid fraction to represent the lipid material of the embryo and the sediment fraction the lipid material of the testa or bran; they named the former embryo and the latter testa oil. These fractions were found to exhibit significant differences in the melting point. The embryo oil had a melting point of from —17 to —21° C. and the testa oil from 60 to 62.5° C.

The high melting point of the testa oil indicated that the ethyl ether extract of the hull or bran contained a material not present in the embryo and endosperm. Further evidence for this fact is found in the work of Yamamota *et al.* (5) and Bidwell, Bopst, and Bowling (9). The former were able to isolate high molecular weight alcohols and small quantities of wax from the unsaponifiable fraction of the testa oil. The latter separated the bran and germ of sorghum grain and corn by mechanical means before ether extraction. They found that the amount of ether soluble material obtained from the bran of sorghum grain was almost eight times greater than from corn, but there was no significant difference in the amount of ether soluble material obtained from the germ. The sorghum grain kernel was found to consist of 6.1% bran, 10.0% germ, and 83.9% endosperm which contained 6.8, 31.5, and 0.7% of ether extractable material respectively. Corn was found to consist of 7.4% bran, 11.5% germ, and 81.1% endosperm which contained 0.89, 34.8, and 1.15% of ether extractable material, respectively. Bidwell *et al.* did not characterize these ether-soluble materials. In the present study the lipid material of the hull was separated from the lipid material in the germ and endosperm and each entity characterized.

Experimental

Separation of the Lipid Material in the Bran from the Lipid Material in the Germ: The separation of the lipid material in the bran from the lipid material in the germ and endosperm was accomplished by fractional solvent extraction. The lipid material of the bran was first removed by extracting the unground grain[3] with Skellysolve B under reflux for one hour. Then the grain was ground and the lipid material of the germ and endosperm removed by extracting with Skellysolve F in a large Soxhlet extractor. On evaporation of the Skellysolve B, a white solid residue with a melting point of 78-82° C. was obtained. The Skellysolve F extract yielded a slightly cloudy, straw-colored oil. Filtration through filter paper at room temperature gave a clear oil. On the basis of the total weight of grain extracted the Skellysolve B extract contained 0.5 and the Skellysolve F extract 2.5% of lipid material. As a means of comparison a sample of white corn[4] was also subjected to fractional solvent extraction. The unground corn was extracted with Skellysolve B, then ground and ex-

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[4]Obtained through the courtesy of E. G. Heyne, Dept. of Agronomy, from The Iowa Experiment Station, Ames, Iowa.
[5]Mazola, Corn Products Refining Company, Argo, Illinois.

tracted with Skellysolve F. The Skellysolve B extract contained 0.01% of semisolid material and the Skellysolve F extract contained 3.98% of clear corn oil.

Lipid Material in the Bran: The white solid residue obtained from the unground sorghum grain was recrystallized from Skellysolve B. A white crystalline material which had a melting point of 81° C. was obtained. On saponification this material yielded 52% of unsaponifiable material, indicating it was a wax. Characterization of this wax according to the method of Chibnall *et al.* (10) yielded a high molecular weight alcohol, an acid, and a hydrocarbon fraction of approximately the same melting point as the counterpart from carnauba wax (Table I). Further characterization of these fractions is now in progress, and the results will be reported in a subsequent paper.

TABLE I.

Comparison of Carnauba and Sorghum Grain Wax.

	Carnauba wax (22)	Sorghum grain wax
Non-saponifiable	54-55%	52%
Acid value	4-7	10.8
Melting points of:		
Wax	85° C.	81° C.
Fatty acids of wax	78-90°	78-82°
Hydrocarbon of wax	58-59°	74-79°
Alcohols of wax	79-87°	82-86°
Acetate der. of alcohols	64-72°	65-69°

Lipid Material in the Germ: The oil obtained from the ground sorghum grain, which had been freed of wax with Skellysolve B, had the following characteristics as determined by standard procedures (11): acid value 3.14, saponification value 181, iodine value 119.0 (Wijs), thiocyanogen value 76.7, acetyl value 16.7, and a refractive index of 1.4718 at 25° C. These characteristics seemed to indicate that the oil obtained from the ground grain was analogous to corn oil in composition (12). Further characterization of this sorghum grain oil was therefore carried out along with corn oil as a means of comparison.

Comparison of Corn and Sorghum Grain Oil: Two hundred and fifty g. each of corn [5] or sorghum grain oil were saponified, diluted with water, and extracted with Skellysolve F to remove the unsaponifiable material. The corn oil yielded 0.91 and the sorghum grain oil 1.88% of unsaponifiable material, respectively. The soaps were then neutralized with dilute hydrochloric acid, and the fatty acids extracted with Skellysolve F, washed with water, dried with sodium sulphate, and freed from solvent. Approximately 200 g. of the fatty acids were diluted with 1800 ml. acetone and subjected to low temperature fractional crystallization. The crystallization chamber was similar to the one described by Quackenbush and Steenbock (13) except that the exterior was not covered with tin, the dry ice chute was larger, and the cover was split into two parts. The split cover facilitated the removal of the precipitate from the Buchner funnel after each filtration.

Upon removal of the acetone under reduced pressure each fraction was freed from the last traces of solvent in a vacuum oven at 110° C. and weighed (Table II). A weighed portion of the fraction obtained at —15° C. and the fatty acids which remained in solution at —60° C. were converted into methyl esters (14) and distilled through an electrically heated packed column at a pressure of from .025 to .200 mm. The saponification equivalents of the methyl ester fractions, the neutralization equivalents of the fractions obtained at —20 to —60° C., as well as the iodine value (Wijs) and thiocyanogen values (15) of all fractions were determined (Table II). With equations suggested by Hilditch (16), Longenecker (17), and Cramer and Brown (18) the percentages of fatty acids were calculated from these data. The theoretical thiocyanogen values for the unsaturated fatty acids and methyl esters that were substituted into these equations were those suggested by Cramer and Brown (18).

Baur and Brown (12) found that one of their distilled methyl ester fractions, which contained methyl hexadecenoate, also contained a small amount of methyl linoleate. In the present study a small amount of linoleic acid could have adhered to the fatty acids which crystallized at —15° C. Spectrophotometric analyses of the distilled methyl esters from the fractions obtained at —15° C. were therefore made according to the method of Mitchell (19) as modified by Baldwin and Longenecker (20).

The presence or absence of linolenic and fatty acids above C_{18} was ascertained by bromination and by an examination of the fraction which remained in solution at —60° C. Approximately one-gram samples of the fatty acids which remained in solution at —60° C. were brominated in ethyl ether at 0° C.; however, no hexabromostearic acid precipitated. A portion of the fraction which remained in solution at —60° C. (neutralization equivalent 293) was made into potassium soaps, extracted exhaustively with Skellysolve F and reconverted into fatty acids. The neutralization equivalent of this Skellysolve F extracted fraction was 282 (theor. for stearic acid 284.4) indicating that the high neutralization equivalent (293) had been due to the presence of non-saponifiable material and not $C_{20\text{-}22}$ fatty acids. Further evidence for the absence of fatty acids greater than C_{18} was found in the low saponification equivalents (Table III) of the distilled methyl esters obtained from the fractions which remained in solution at —60° C.

Results: Sorghum grain was found to contain 0.5% wax and 2.5% oil. This was approximately 50 times more wax and two-thirds as much oil as found

TABLE II.

Fractional Crystallization of the Fatty Acids from Corn and Sorghum Grain Oil.

	Corn Oil (Iodine Number = 124.8)				Sorghum Grain Oil (Iodine Number = 119.0)			
Fraction	Weight	Iodine No.	Thiocyanogen No.	Neutralization Equiv.	Weight	Iodine No.	Thiocyanogen No.	Neutralization Equiv.
—15° C.	19.00	.....	.....	.....	27.50	.....	.....	.....
—20° C.	.....	.....	.....	.....	5.40	96.8	64.6	280
—30° C.	6.30	88.4	67.1	280	74.00	125.4	90.0	283
—40° C.	36.36	118.1	90.5	282	35.84	130.6	90.2	282
—50° C.	37.15	138.6	93.2	281	27.90	148.8	95.5	281
—60° C.	35.70	155.2	96.3	281	29.14	161.2	96.8	281
Filtrate	65.90	159.4	96.4	293	23.15	164.0	96.8	292
Total	200.41	.....	.....	.....	222.93	.....	.....	.....

TABLE III.

Fractional Distillation of Methyl Esters from Corn and Sorghum Grain Oil.

Fraction	Corn Oil				Sorghum Grain Oil			
	Weight	Iodine No.	Thiocyanogen No.	Saponification Eq.	Weight	Iodine No.	Thiocyanogen No.	Saponification Eq.
—15° C.								
1	3.3	2.30	1.20	267.5	4.4	0.77	0.50	269.0
2	2.8	2.75	1.74	268.5	2.9	.78	.55	268.7
3	5.6	3.43	2.52	267.5	5.9	.98	.59	269.4
4	0.5	4.89	3.45	268.0	8.4	1.28	.92	278.0
5	2.1	8.28	5.26	284.0	2.3	2.57	1.52	292.0
Residue[1]	0.5	8.25	.....	.....	1.1	17.50	.....	.....
Total	14.8				25.0			
—60° filtrate								
1	3.5	155.2	88.3	287.8	3.4	157.5	90.1	289.5
2	10.3	158.1	89.7	291.0	4.9	162.3	90.6	296.0
3	2.1	156.5	89.2	297.0	2.9	163.8	92.2	294.8
4	0.5	153.6	87.2	296.6	4.8	165.0	92.2	298.0
Residue	0.8	98.5	75.7	606.0[2]	1.4	88.4	70.0	670.0
Total	17.2				17.4			

[1]Added to fraction 5 in calculation.
[2]High value due to unsaponifiable material which had not been extracted prior to distillation.

in a sample of white corn extracted under identical conditions. Sorghum grain wax was found to be similar in composition to carnauba wax, and sorghum grain oil similar to corn oil. However, sorghum grain oil contained more oleic and stearic, and less linoleic, myristic, and hexadecenoic acid than corn oil (Table IV). Neither oil contained linolenic acid or fatty acids above C_{18}.

TABLE IV.

Comparison of the Fatty Acids in Corn and Sorghum Grain Oil.

Fatty Acids	Corn Oil		Sorghum Grain Oil
	Baur and Brown Wt.%	Present Results Wt.%	Present Results Wt.%
Myristic	0.1	0.5	0.2
Palmitic	8.1	9.7	8.3
Stearic	2.5	3.6	5.8
Hexadecenoic	1.2	.2	.1
Oleic	30.1	30.4	36.2
Linoleic	56.3	55.6	49.4
Above C_{18}	1.7	.....	.....

In agreement with Baur and Brown (12) it was found that the fractions which contained methyl hexadecenoate also contained methyl linoleate. Spectrophotometric analyses and calculations involving the thiocyanogen and iodine values indicated that from 0.3 to 1.3% of methyl linolate was present in these fractions. When the presence of this linoleic acid was taken into account, the results indicated that the corn oil studied in the present paper contained less hexadecenoic acid than the one studied by Baur and Brown (Table IV).

Discussion

Previous characterizations of the oil in sorghum grain (7,16) have been complicated by the presence of varying amounts of wax. Furthermore the testa oil reported by previous workers (5,8) must have been embryo oil containing a large amount of wax. In the present study it was found that contamination of the oil with wax could be avoided by fractional solvent extraction. The wax was first removed by extracting the whole grain with Skellysolve B. The grain was then ground and the oil removed by extracting with Skellysolve F.

When the wax was not removed from the surface of the grain before grinding, a translucent semisolid extract was obtained (5,6,8). Separation of this material by centrifugation was not successful (7). However, Barham *et al.* (1) were able to separate the wax from the oil by repeated crystallization of the semisolid material from Skellysolve B.

In the manufacture of starch on a commercial basis, the bran and germ are by-products. The analyses of Bidwell *et al.* (9) indicated that the lipid material in sorghum grain was concentrated in the bran and germ. Therefore the yield of wax, per pound of material extracted, could probably be increased by extracting the hulls or bran and the yield of oil increased by pressing the germ.

In the present characterization of corn and sorghum grain oil low temperature fractional crystallization of the fatty acids was employed in order to remove the bulk of the highly unsaturated fatty acids before fractional distillation of the methyl ester. Hilditch and Riley (21) have recently recommended this procedure as a means of determining the component acids in fats which contain oleic and linoleic acids as major components.

Summary

Sorghum grain was found to contain approximately 50 times more wax and two-thirds as much oil as corn. The wax, which had properties similar to carnauba wax, could be removed by extracting the unground grain with hot solvent.

Sorghum grain oil was found to be similar to corn oil in composition. Sorghum grain oil had the following characteristics: unsaponifiable matter 1.88%, acid value 3.14, saponification value 181, iodine value 119.0, thiocyanogen value 76.7, acetyl value 16.7, and a refractive index of 1.4718 at 25° C. The mixed fatty acids from the oil contained 36.2% oleic, 49.4% linoleic, 8.3% palmitic, 5.8% stearic, 0.2% myristic, and .1% hexadecenoic acid.

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Abstracts

Oils and Fats

Edited by
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REPORT ON ETHER EXTRACT IN FISH. M. D. Voth (Food and Drug Admin., Boston, Mass.). *J. Assoc. Official Agr. Chem. 29,* 46-9 (1946). Collaborative work indicated that the fat content determined by digestion with HCl followed by extraction with ether agrees closely with that obtained by the Stansby and Lemon extractor.

SOUTH AFRICAN FISH PRODUCTS XX. MODE AND DEGREE OF FAT STORAGE IN THE CAPE JOHN DORY (ZEUS CAPENSIS C. AND V.) IN RELATION TO CHEMICAL COMPOSITIONS OF THE LIVER AND BODY FATS. M. M. Black, W. S. Rapson, H. M. Schwartz, and N. J. Van Rensburg. (Univ. Cape Town, So. Africa). *J. Soc. Chem. Ind. 65,* 13-15 (1946). Component acid analyses have been carried out on body and liver oils from the Cape John Dory (*Z. capensis* C. and V.) in fat or thin condition. In both liver and body, increase in fat content of the fish results in an increase in the content of the highly unsaturated C_{20}, C_{22}, and C_{24} acids in the oil, and a decrease in the degree of average unsaturation of the C_{18} and C_{20} acids. In the liver the latter effect is dominant and therefore the I value of the liver oil tends to decrease with increase in fat content of fish; in the body, however, the former effect prevails and increase in I value of the body oil results.

THE VITAMIN A AND CAROTENE CONTENT OF MARKET BUTTER PRODUCED IN KANSAS. D. B. Parrish, W. H. Martin, F. W. Atkeson, and J. S. Hughes (Kan. Agr. Exper. Sta., Manhattan). *J. Dairy Sci.* 29, 91-9 (1946). The 1944 mean annual vitamin A potency of Kansas butter was 15,100 I.U. per pound. The mean for the period December to April was 11,050 I.U. per pound, and from May to November, 17,700 I.U. per pound. In the above periods carotene accounted for 19.6%, 14.9%, and 21.4% of the total vitamin A potency of Kansas butter. The vitamin A and carotene content of butter produced in different areas of the state and during different months of the year varied with the pasture available. When little or no pasture existed the values for vitamin A and carotene dropped.

THE HIGHER FATTY ALCOHOL ESTERS OF GALLIC ACID. S. G. Morris and R. W. Riemenschneider (Eastern Regional Res. Lab.). *J. Am. Chem. Soc. 68,* 500-1 (1946). The normal hexyl, octyl, dodecyl, tetradecyl, hexadecyl, and octadecyl esters of gallic acid have been been prepared and characterized. They were obtained by first preparing the corresponding esters of 4,5,6-tris-(benzyloxy)-benzoic acid and then debenzylating them by catalytic hydrogenation.

THE NUTRITIVE VALUE OF TOBACCO-SEED OIL. K. E. Rapp, J. T. Skinner, and J. S. McHargue (Ky. Agr. Exper. Sta., Lexington). *J. Nutr. 31,* 273-82 (1946). When tobacco-seed oil was fed to rats at levels of 5, 15, and 30% of the respective rations it gave an average coefficient of digestibility of 97.9 as compared with 99.1 and 98.2 for cottonseed oil and butterfat, respectively. With paired feeding of refrigerated rations containing 30% of tobacco-seed oil and butterfat, respectively, growth rates of rats did not differ significantly. When fed *ad lib.* the difference in consumption of the 2 rations produced a greater rate of growth in rats fed butterfat. Of 6 rats fed refrigerated ration and 4 animals fed non-refrigerated ration containing 30% tobacco-seed oil for 5 weeks, during the period when growth is usually maximum, all proved to be fertile upon reaching maturity.

FATTY CONSTITUENTS OF TUBERCLE BACILLI AS GROWTH INHIBITORS OF THE SAME BACILLI. Buu-Hoi (École polytechnique, Paris). *Nature 156,* 392 (1945). A mixture of fat acids obtained from dead tubercle bacilli of a virulent strain of human origin was converted through the acid chlorides and amides into a mixture of primary amines. Although the initial material and the amides were practically inactive, the mixture of amines, as HCl salts, was bacteriostatic against tubercle bacilli growing on synthetic media in 1-10,000 dilution. Synthetic fat acid amines of the formula $R(R_2')C.\text{-}NR_2''$ were also found to be bacteriostatic against acid fast bacteria. (*Chem. Abs.* 40, 373.)

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RESISTANCE TO EXTREME TEMPERATURE IN CONNECTION WITH DIFFERENT DIETS. L. P. Dugal (Univ. Mon-