THE COMPOSITION OF FATTY ACIDS AND GLYCERIDES OF CORN OIL AND ITS WINTERIZATION FILTER CAKE

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The characteristics and composition of corn oil have been studied by many authors. In two recent studies, the one by Lofland *et al.*[1] and the other by Sniegowski and Bardwin,[2] a number of corn samples were analyzed for oil content and the refractive index, iodine value and fatty acid composition of oil, and the equations showing the relationship between oil content, iodine value and the contents of saturated, oleic and linoleic acids were derived by statistical analysis of the data. According to Lofland *et al.*, oil content, iodine value and the percentages of saturated, oleic and linoleic acids in the total fatty acids for 392 samples had the following ranges, respectively: 1.13-13.80%, 88.4-147.4, 0-21.3%, 16.5-75.9% and 15.7-67.6%. Doerschuk and Daubert[3] subjected corn oil to a detailed fractionation and found the glyceride composition to be 2.2% of GS_2U, 40.3% of GSU_2 and 57.5% of GU_3 (G = glyceryl radical, S = saturated acids, U = unsaturated acids). Kartha[4] reported the contents of GS_2U, GSU_2 and GU_3 in the glycerides of corn oil to be 12, 43 and 45 mol.%, respectively. It should be mentioned herewith that while previous studies on corn oil have been done mostly with oil samples from the corns grown in the United States of America, South African corns also have recently been imported into our country. Iodine value of South African corn oil appears generally a little lower than that of American corn oil.

Corn oil for edible purpose is commonly winterized. The composition of the fatty acids and glycerides of winterization filter cake has not been fully studied. Shriner *et al.*[5] obtained about 1% of crystalline wax of m.p. 81°-82°C from the winterization filter cake of corn oil, and indicated the presence of *n*-tetracosanoic and iso-behenic acids among the fatty acid components and myricyl alcohol among the alcohol components in this wax.

In this paper, the results of our studies on the fatty acid and glyceride compositions of an American yellow dent corn oil, a South African white dent corn oil and their winterization filter cakes are reported.

Experimental

1. Characteristics of oil samples. The samples of corn oil and its winterization filter cake were supplied by the courtesy of the Nihon Shokuhin Kako Co., Ltd. They were prepared at the plant of this company in Handa. Crude oil was

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pressed by expeller separately from the germs of American yellow dent corns and from the germs of South African white dent corns. The crude oil was then freed from gums by filtration, refined with alkali and bleached with activated clay and carbon. The refined and bleached oil was then subjected to the winterization at the temperatures ranging from 5°C to −2°C. Characteristics of the refined and bleached oil and its winterization cake are shown in Table 1.

TABLE 1. Characteristics of Corn Oil and Its Winterization Filter Cake

	American yellow dent		South African white dent	
	Refined and bleached oil	Winterization filter cake	Refined and bleached oil	Winterization filter cake
Appearance at ordinary temp.	Pale yellow, clear	Pale yellow, turbid	Pale yellow, clear	Pale yellow, turbid
Refractive index	1.4737 (20°C)	1.4654 (40°C)	1.4724 (20°C)	1.4638 (40°C)
Viscosity at 30°C (Redwood, sec.)	181	—	184	—
Acid value	0.42	—	0.41	—
Saponif. V.	192.2	192.1	191.7	191.5
Iodine V. (Wijs)	126.6	120.2	114.6	104.6
Peroxide V. (AOCS method)	25.7	—	10.1	—
Unsaponifiable matter (%)	1.21	1.12	1.46	1.26

Notes: Peroxide values were determined on June 16, 1956, while the oil samples were received in March and April, 1956.

2. The Characteristics and composition of fatty acids. The fatty acids freed from unsaponificable matter were separated from oil samples in the usual way. The solid acids in fatty acids were determined by the lead salt ethanol method, and the content of saturated acids were calculated from the amount and iodine

TABLE 2. The Characteristics and Composition of Fatty Acids

	American yellow dent		South African white dent	
	Refined and bleached oil	Winterization filter cake	Refined and bleached oil	Winterization filter cake
n_D^{40}	1.4573	1.4567	1.4562	1.4552
Neutralization V.	200.7	200.9	200.7	200.9
Iodine V.	131.7	125.3	120.2	110.0
Solid acids (%)	11.4	15.8	15.9	24.1
I.V. of solid acids	4.4	6.9	6.6	5.2
Saturated acids (%)	10.8	14.6	14.8	22.7
Oleic acid (%)	32.8	32.2	37.5	32.9
Linoleic acid (%)	56.4	53.2	47.7	44.4
Spec. extinc. coeff. of alkali-isomerized acids at 232 mμ	52.91	49.62	45.13	42.17
Saturated acids (%)	11.9	15.3	16.0	24.1
Oleic acid (%)	30.7	30.8	35.0	30.1
Linoleic acid (%)	57.4	53.9	49.0	45.8
Saturated acids (%)*	11.35	14.95	15.4	23.4
Oleic acid (%)*	31.75	31.5	36.25	31.5
Linoleic acid (%)*	56.9	53.55	48.35	45.1

Notes: * The average of the figures obtained by the determination of solid acids and by the spectrophotometric measurement.

value of solid acids by assuming the unsaturated acids in solid acids wholly as oleic acid. Oleic and linoleic acids were calculated from the iodine value of total fatty acids and the percentage of saturated acids. Furthermore, linoleic acid content was determined by the ultraviolet absorption measurement of the alkali-isomerized product of fatty acids obtained under the condition of 6.5% KOH-glycol, 180°C and 25 minutes with a current of nitrogen.[6] The fatty acid composition was also calculated from the iodine value of total fatty acids and the linoleic acid content. The results are shown in Table 2.

3. Glyceride composition. The determination of glyceride composition was carried out by Kartha's method.[7] About 5 g of oil was dissolved in 200 cc of acetone and 20 cc of glacial acetic acid, and 40 g of powdered potassium permanganate was gradually added in small portions. The mixture was refluxed for four hours until the oxidation has been completed. After the removal of acetone by distillation, about 150 cc of water was added to the residue. Sodium bisulfite and dilute sulfuric acid were added in small portions to the aqueous mixture while heating on a water bath in order to reduce the excess of permanganate and manganese oxides. The aqueous mixture was then extracted with one liter of ether followed by a subsequent extraction with 700 cc of ether. The ether-solution was washed several times with water until the washings have become almost free from acid. The ether was then distilled off, and the residue was suspended in about 200 cc of water and neutralized with a 5% solution of sodium carbonate. The solution was then diluted with water to 500 cc, and 30 cc of a 10% solution of ammonium chloride was added. A 15% solution of magnesium sulfate was then added until no more precipitate of magnesium salts formed. After the precipitate (I) was allowed to settle for 10 minutes, it was filtered on a filter paper, washed four times with water using 30 cc each time, and then heated on a water bath with dilute sulfuric acid until all of the magnesium salts were decomposed. After cooling, the fatty matter separated was extracted with ether, and the ether solution was washed with water until the washings have become free from acid. The ether was then distilled off and the residue was weighed. This residue was saponified, and the saponification product was acidified with dilute sulfuric acid. The free fatty acids thus obtained were treated in the same way as for the determination of saturated acids by Bertram's method, and the saturated acids free from azelaic acid were separated and weighed, and their melting point, neutralization value and iodine value were determined.

The filtrate separated from the precipitate (I) was acidified with dilute sulfuric acid and the fatty matter was extracted from the acidified solution with ether, and weighed. The saturated acids were separated from this fatty matter in the same way as described for the precipitate (I) and weighed, and their melting point and neutralization value were determined.

The fully saturated glycerides were absent in all oil samples, since no crystalline glycerides separated when 10 g of oil was dissolved in 30 cc of acetone and the solution was kept at 25°-26°C for three days. The results of experiments and the glyceride compositions calculated from the observed data are shown in Table 3. For the sake of comparison, the glyceride compositions calculated from the fatty acid compositions (Table 2) by Kartha's "restricted random distribution" theory are shown in Table 4.

TABLE 3. Glyceride Composition

	American yellow dent		South African white dent	
	Refined and bleached oil	Winterization filter cake	Refined and bleached oil	Winterization filter cake
Sample (g)	5.2152	5.5500	5.2511	5.3234
Fatty matter from the precipitate of Mg-salts (*a*) (g)	0.6512	1.3834	1.0142	1.7864
Saturated acids from (*a*) (g)	0.3245	0.6486	0.4971	0.9509
Saturated acids from (*a*) I.V.	0.6	0.6	0.9	0.7
Saturated acids from (*a*) N.V.	208.7	208.9	208.7	209.2
Saturated acids from (*a*) m.p. (°C)	53-53.5	53-53.5	53-53.5	53-53.5
Unoxidized GS_2U (g)	0.0079	0.0134	0.0151	0.0225
Unoxidized GS_2U Saturated acids (g)	0.0050	0.0084	0.0095	0.0141
GS_2A (g)	0.2115	0.3272	0.3052	0.7858
GS_2A Saturated acids (g)	0.1489	0.2303	0.2149	0.5524
GSA_2 (g)	0.4397	1.0428	0.6939	0.9781
GSA_2 Saturated acids (g)	0.1732	0.4099	0.2727	0.3844
Fatty matter from the filtrate of Mg-salts (*b*) (g)	4.3818	3.9549	4.1864	3.3442
Saturated acids from (*b*) (g)	0.2815	0.1486	0.2720	0.2510
Saturated acids from (*b*) N.V.	209.0	208.8	208.9	209.2
Saturated acids from (*b*) m.p. (°C)	53-53.5	53-53.5	53-53.5	53-53.5
GSA_2 (g)	0.7170	0.3791	0.6925	0.5654
Glyceride (mol.%) (Saturated acids)	12.6	15.6	15.9	24.6
GS_3	0	0	0	0
GS_2U	4.6	7.0	7.0	17.4
GSU_2	28.4	32.8	33.8	39.1
GU_3	67.0	60.2	59.1	43.5

Notes: A = azelaic acid

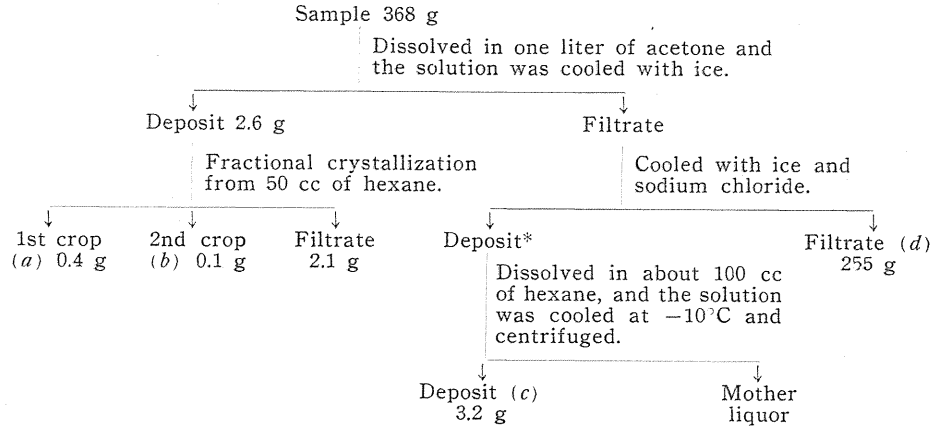
TABLE 4. Glyceride Composition Calculated from the Fatty Acid Composition Based on the "Restricted Random Distribution" Theory

	Refined and bleached oil			
	American yellow dent		South African white dent	
	A	*B*	*A*	*B*
GS_3 (mol.%)	0	0	0	0
GS_2U (mol.%)	3.5	4.4	6.4	6.9
GSU_2 (mol.%)	26.6	28.8	33.1	34.1
GU_3 (mol.%)	69.9	66.8	60.5	59.0

Notes: The figures in the column *A* were calculated from the fatty acid composition based on the determination of saturated acids by the lead salt ethanol method, while those in the column *B* based on the linoleic acid content determined by the spectrophotometric method.

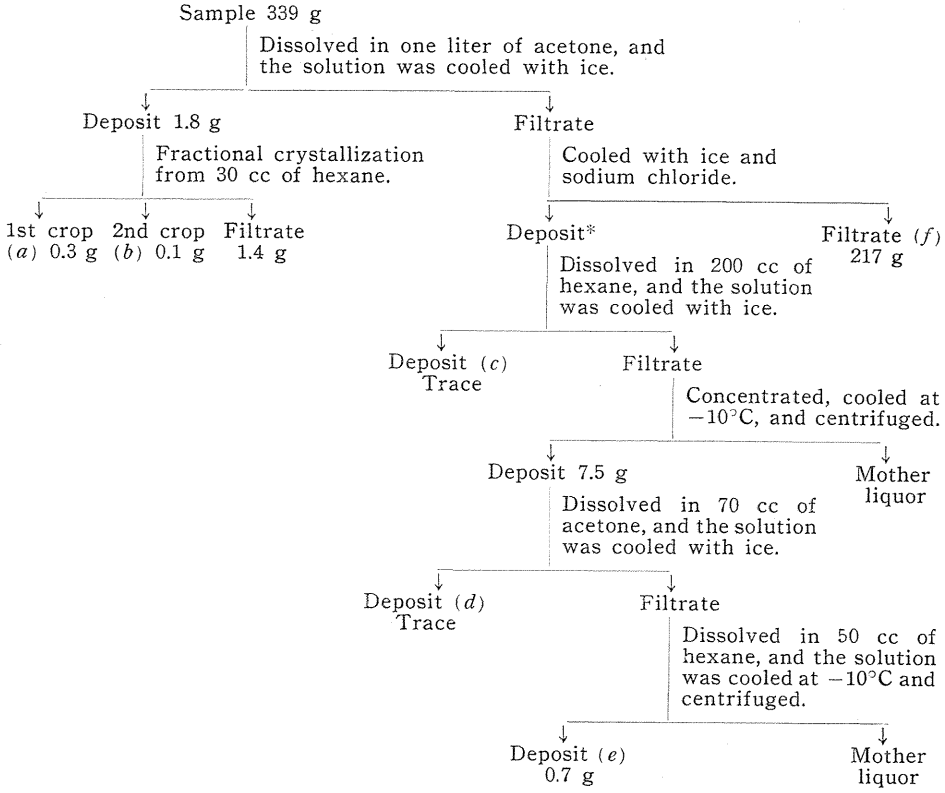
4. Examination of solid components in winterization filter cake. Each sample of winterization filter cake was fractionated as shown in Tables 5 and 6 in order to separate solid components.

TABLE 5. The Solid Components of the Winterization Filter Cake from American Yellow Dent Corn Oil



* This deposit was still contaminated with a large proportion of liquid due to the difficulty in filtration.

TABLE 6. The Solid Components of the Winterization Filter Cake from South African White Dent Corn Oil

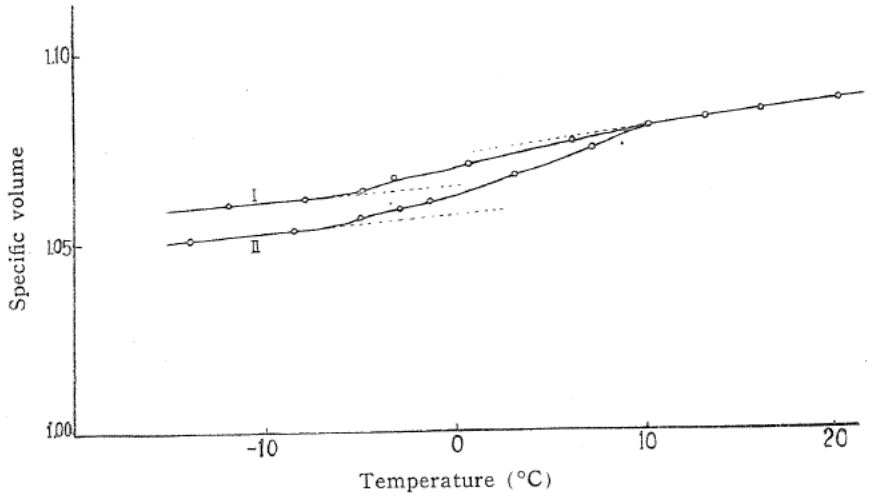


* This deposit was contaminated with a large proportion of liquid due to the difficulty in filtration.

The 1st crop (*a*) in Table 5 had m.p. 56.5°–71°C, S.V. 166.8 and unsaponifiable matter 20.07%. The fatty acids from this crop showed m.p. 64°-65.5°C and Neutr. V. 174.6 after recrystallization from ethanol. The unsaponifiable matter from this crop had m.p. 75°–77.5°C after recrystallization from ethanol. The 2nd crop (*b*) in Table 5 had m.p. 50.5°–58°C and I.V. 51.2. The deposit (*c*) in Table 5 had S.V. 189.2 and I.V. 109.6, and its cloud point was below 3°C. The filtrate (*d*) in Table 5 remained clear even after cooling at 0°–1°C for five hours.

The 1st crop (*a*) in Table 6 had m.p. 58°–74.5°C, S.V. 139.5 and unsaponifiable matter 33.84%. The fatty acids from this crop had m.p. 71°–72°C and Neutr. V. 155.7 after recrystallization from ethanol. The unsaponifiable matter from this crop, recrystallized from ethanol, had m.p. 76.5°–79°C. The 2nd crop (*b*) in Table 6 had m.p. 50.5°–62°C and I.V. 50.4. The deposit (*c*) in Table 6, recrystallized from acetone, showed m.p. 52.5°–54°C. The deposit (*d*) in Table 6 had m.p. 47.5°-49°C, and the deposit (*e*) in Table 6 had S.V. 190.6, I.V. 91.7 and cloud point 4.5°C. The filtrate (*f*) in Table 6 remained clear after cooling at 0°–1°C for five hours.

5. Dilatometry of winterization filter cake. While the foregoing results indicate that the components which are solid at ordinary temperature are contained only in a minor amount in both samples of winterization filter cake, the specific volumes of both samples at varying temperatures were determined by using a dilatometer in order to know the content of solid components at lower temperatures. The results are shown in Fig. 1. The content of solid components at about 0°C was estimated to be about 30% for the sample from American yellow dent and about 60% for the sample from South African white dent, although the melting ranges of both samples were found too wide to permit an accurate determination of the content of solid components at a given temperature.



I Winterization filter cake from American yellow dent oil.
II Winterization filter cake from South African white dent oil.

FIG. 1. Specific volume-temperature curve for winterization filter cake.

Discussion

The American yellow dent oil used in this study is considered to be a typical one as such in its iodine value and fatty acid composition, whereas the South African white dent oil has a considerably lower iodine value and its fatty acids contain a larger proportion of saturated acids and a smaller proportion of linoleic acid as compared with the American yellow dent oil. The glycerides of the American yellow dent oil contain GS_2U and GSU_2 in a smaller proportion and GU_3 in a larger proportion as compared with those of the South African white dent oil. The glyceride compositions of both oils estimated by the permanganate oxidation method coincide, on the whole, with those calculated from the fatty acid compositions by applying Kartha's "restricted rondom distribution" theory.

The winterization filter cake from the American yellow dent oil contains saturated acids in a larger proportion, oleic acid in nearly same proportion and linoleic acid in a smaller proportion among the fatty acid components, and GS_2U and GSU_2 in a larger proportion and GU_3 in a smaller proportion among the glyceride components as compared with the oil before winterization. The winterization filter cake from the South African white dent oil contains saturated acids in a remarkably larger proportion and oleic and linoleic acids in a smaller proportion among the fatty acid components, and GS_2U and GSU_2 in a larger proportion and GU_3 in a smaller proportion among the glyceride components as compared with the oil before winterization. On the whole, the differences between the fatty acid and glyceride compositions of the whole oil and those of the winterization filter cake are more marked for the South African white dent than for the American yellow dent.

The 1st crops in Tables 5 and 6 contain wax esters besides glycerides, and both high melting fatty acids and unsaponifiable components are present in these wax esters. However, the major components of the total saturated acids are considered to be palmitic and stearic acids, and the saturated acids higher than stearic are contained only in a minor amount, since the neutralization value of the total saturated acids is found to be about 209 for all oil samples used in this study. The 2nd crops in Tables 5 and 6 are recognized to contain GS_2U from their iodine values. The yields of these crops, however, are very low. The solid glycerides of GS_2U type could not be separated in a considerable amount in this study, though these glycerides are possibly contained in a considerable amount in the winterization filter cake.

Since the winterization filter cakes contain a relatively large proportion of liquid components even at about 0°C, especially the winterization filter cake from the American yellow dent oil contains roughly about 70% of liquid components at about 0°C, it seems possible to recover a further amount of liquid components from the winterization filter cakes.

Summary

The compositions of the fatty acids and glycerides (GS_3, GS_2U, GSU_2 and GU_3) of (I) refined and bleached oil from American yellow dent corn germs, (II) winterization filter cake from I, (III) refined and bleached oil from South African white dent corn germs, and (IV) winterization filter cake from III were determined. The contents (%) of saturated, oleic, and linoleic acids in the total fatty

acids were found to be 11.35, 31.75, 56.9 for I; 14.95, 31.5, 53.55 for II, 15.4, 36.25, 48.35 for III; 23.4, 31.5, 45.1 for IV. The contents (mol.%) of GS_3, GS_2U, GSU_2 and GU_3 were found to be 0, 4.6, 28.4, 67.0 for I; 0, 7.0, 32.8, 60.2 for II; 0, 7.0, 33.9, 59.1 for III; 0, 17.4, 39.1, 43.5 for IV. The glyceride compositions of both samples of refined and bleached oil approximate to the glyceride compositions calculated from the fatty acid compositions by applying Kartha's "restricted rondom distribution" theory.

The fractionation of the winterization filter cakes gave a minor amount of crystalline fractions containing wax esters besides saturated glycerides. From these fractions, high melting fatty acid and unsaponifiable components were separated. The winterization filter cakes were found to contain a relatively large proportion of liquid components even at about 0°C.

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