

[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY,
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THE CHEMICAL COMPOSITION OF PEANUT OIL.

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The qualitative composition of peanut oil has been quite definitely established but only one attempt to determine its quantitative composition is reported. Caldwell¹ identified palmitic acid. Nobody seems to have definitely isolated and identified stearic acid. Hehner and Mitchell² obtained from the mixed fatty acids 7 % of fatty acid crystals melting at 67° which they assumed to be stearic acid. However, Meyer and Beer³ have shown that the fatty acid crystals obtained by the Hehner and Mitchell method consist of a mixture of arachidic and lignoceric acids instead of stearic acid. Gössmann⁴ was the first to prove the presence of arachidic acid and Kreiling⁵ the first to detect lignoceric acid. Gössmann and Scheven,⁶ Caldwell and Gössmann,⁷ and Schröder⁸ claim to have found hypogaecic acid; however, their work has been repeated by a number of other investigators and no one has been able to confirm their statements (Schön,⁹ Kreiling,¹⁰ Meyer and Beer,¹¹ Bodenstein,¹² Hazura and Grussner,¹³ Heiduschka and Felser).¹⁴ Hazura and Grussner pointed out that peanut oil contains another unsaturated acid in addition to oleic acid, *i. e.*, linolic acid; and Farnsteiner¹⁵ analyzed the bromine addition products of the unsaturated acids and calculated the amount of linolic acid as about 6% of the total fatty acids. Finally, Heiduschka and Felser¹⁶ made an investigation of the quantitative composition of the fatty acids and report the following results: lignoceric acid, 1.9%; arachidic acid, 2.3%; stearic acid, 4.5%; palmitic acid, 4.0%; oleic acid, 79.9%; linolic acid 7.4%. Our knowledge of the general character of peanut oil led us to doubt the

¹ Caldwell, *Ann.*, **101**, 97 (1857).

² Hehner and Mitchell, *Analyst*, **21**, 328 (1896).

³ Meyer and Beer, *Monatsh.*, **34**, 1195 (1913).

⁴ Gössmann, *Ann.*, **89**, 1 (1854).

⁵ Kreiling, *Ber.*, **21**, 880 (1888).

⁶ Gössmann and Scheven, *Ann.*, **94**, 230 (1855).

⁷ Caldwell and Gössmann, *ibid.*, **99**, 305 (1856).

⁸ Schröder, *ibid.*, **143**, 22 (1867).

⁹ Schön, *ibid.*, **244**, 253 (1888); and *Ber.*, **21**, 878 (1888).

¹⁰ Kreiling, *loc. cit.*

¹¹ Meyer and Beer, *loc. cit.*

¹² Bodenstein, *Ber.*, **27**, 3397 (1894).

¹³ Hazura and Grussner, *Monatsh.*, **10**, 242 (1890).

¹⁴ Heiduschka and Felser, *Z. Nahr. Genussm.*, **38**, 242 (1919).

¹⁵ Farnsteiner, *ibid.*, **2**, 23 (1899).

¹⁶ Heiduschka and Felser, *loc. cit.*

accuracy of these figures and to undertake a thorough investigation of the composition of peanut oil.

The two samples of oil used in this investigation were expressed in this laboratory by means of an oil expeller. The oil was not refined. One sample was obtained from the white Spanish type peanuts which had been grown in South Carolina, the other sample was pressed from the Virginia type, grown in Virginia.

Chemical and Physical Characteristics.—The determinations, the results of which are reported in Table I, were made in order to establish the identity of the samples. The results fall within the limits of those reported in the literature. The Virginia oil has a higher iodine number than the Spanish, while the iodine number of the unsaturated acids of the Virginia oil is lower than that of the unsaturated acids of the Spanish oil. The Virginia oil has a higher percentage of unsaturated acids and a lower percentage of saturated acids than the Spanish oil. The percentages of saturated and unsaturated acids, determined by the lead-salt—ether method, have been corrected for the small amounts of unsaturated acids, as indicated by the iodine number of the saturated acids, that are weighed up with the saturated acids.¹

TABLE I.
PEANUT OIL.
Chemical and physical characteristics.

	From Spanish type peanuts.	From Virginia type peanuts.
Specific gravity 25°/25°.....	0.9148	0.9136
Iodine number (Hanus).....	90.1	94.8
Saponification value.....	188.2	187.8
Unsaponifiable matter (%).....	0.22	0.27
Acid value.....	0.12	0.03
Acetyl value.....	8.7	9.50
Reichert Meissl number.....	0.27	0.21
Polenske number.....	0.12	0.29
Saturated acids, % (determined).....	21.4 ^a	17.4 ^b
Unsaturated acids, % (determined)....	73.4	77.7
Saturated acids, % (corrected).....	20.6	16.4
Unsaturated acids, % (corrected).....	74.6	78.7
Iodine number of unsaturated acids	121.8	118.2

^a Iodine number 4.8

^b Iodine number 7.1

Unsaturated Acids.—The bromine addition derivatives of the unsaturated acids were prepared and analyzed as follows.² The unsaturated acids were dissolved in absolute ether and cooled to about 15°. Bromine was added slowly to the solution and the mixture allowed to stand for

¹ THIS JOURNAL, 42, 11, 2398 (1920).

² Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes." Fifth ed., 1, 573.

2 hours at 10° to 15°. No hexabromide, the bromo derivative of linolenic acid which is insoluble in ether, was found. The excess of bromine was removed from the ethereal solution by washing with an aqueous solution of thiosulfate. After drying with anhydrous sodium sulfate the ether was distilled off and the residue dissolved in 100 cc. of petroleum ether. The petroleum ether solution was allowed to stand overnight in the ice box and then the linolic tetrabromide which had precipitated was removed by filtration through a Gooch crucible. The filtrate was reduced to about one-half its original volume, cooled in the ice box and a second crop of tetrabromide crystals obtained and removed by filtration. The filtrate was evaporated to dryness and weighed. The bromine content of the residue was determined by boiling a small sample with conc. nitric acid and silver nitrate. From these data and the theoretical bromine contents of linolic tetrabromide (53.33 %) and oleic dibromide (36.18 %) the percentages of tetrabromide and dibromide in the residue were calculated.

The data of the analyses of the bromo derivatives are given below.

	Spanish type.	Virginia type.
Sample of unsaturated acids, g.....	3.4863	3.5238
Linolic tetrabromide insoluble in petroleum ether, m. p. 113-114, g.....	1.3993	1.1642
Residue (dibromide and tetrabromide), g...	4.6766	4.9682
Bromine content of residue, %.....	39.73	39.11
Dibromide in residue, %.....	79.30	82.92
g.	3.7093	4.1196
Tetrabromide in residue, %.....	20.70	17.08
g.	0.9683	0.8486
Total tetrabromide found, g.....	2.3676	2.0128
Linolic acid equivalent to tetrabromide, g... %	1.1049	0.9393
Oleic acid equivalent to dibromide, g.... %	31.69	26.66
	2.3665	2.6283
	67.88	74.59

The percentage composition of the unsaturated acids, also the amounts of oleic and linolic acids and their glycerides in the oil are given below.

	Spanish oil.		Original oil.	Glycerates in original oil.
	Found. %	Calculated to basis of 100 %.		
Oleic acid.....	67.88	68.2	50.6	52.9
Linolic.....	31.69	31.8	23.6	24.7
Total.....	99.57	100.0	74.2	77.6
	Virginia oil.			
Oleic acid.....	74.59	73.7	58.0	60.6
Linolic.....	26.66	26.3	20.7	21.6
Total.....	101.25	100.0	78.7	82.2

The calculated iodine numbers of the unsaturated acid mixtures having the percentage compositions represented in the second column are 1191, and 114.1 respectively. These values are comparable with the observed iodine numbers, 121.8 for the Spanish oil and 118.2 for the Virginia oil.

Tests for Hypogaecic Acid, $C_{16}H_{30}O_2$.—This acid was stated by Gössmann and Scheven, Caldwell and Gössmann, and Schröder to occur in peanut oil. Schröder's report would indicate that it occurs in fairly large amounts since he studied the properties and made several derivatives of the acid which he separated from peanut oil. However, no one else has been able to detect this acid in peanut oil. Bodenstein¹ prepared hypogaecic acid synthetically from stearolic acid. The constitutional formula $CH_3(CH_2)_7CH=CH(CH_2)_5COOH$ was assigned. It melted at 33° to 34° and absorbed two atoms of bromine per molecule, agreeing with the properties of the acid obtained by Schröder. However, Bodenstein was not able to detect hypogaecic acid in peanut oil. The method by which Gössmann and Scheven and Caldwell and Gössmann obtained hypogaecic acid from peanut oil is briefly as follows. The sodium salts of the fatty acids, obtained by saponifying the oil with sodium hydroxide, were decomposed with hydrochloric acid. The free fatty acids were dissolved in alcohol and to this solution magnesium acetate and ammonia were added as long as a precipitate was formed. The precipitate was filtered off. An alcoholic solution of lead acetate and ammonia was added to the filtrate which was then put aside for several days. The precipitate was removed and extracted with ether in a stoppered cylinder. The lead salts in the ether solution were decomposed with hydrochloric acid and removed by washing with water. The ether solution was concentrated to a small volume and on cooling a yellow crystalline precipitate was obtained which, after recrystallizing from alcohol, melted at 34° – 35° and had the composition $C_{16}H_{30}O_2$.

Schröder's procedure is different. The free fatty acids obtained by decomposing the sodium salts with hydrochloric acid were dissolved in the smallest amount possible of hot alcohol. On cooling crystalline plates of "arachidic acid" were obtained. On concentrating the filtrate in an atmosphere of hydrogen a semi-solid mass resulted which was pressed between filter paper and dissolved in hot alcohol. This solution was concentrated and cooled several times with removal of the crops of crystals until on cooling no crystals separated. The alcohol was evaporated in an atmosphere of hydrogen and yielded small white crystals of pure hypogaecic acid melting at 33° . He prepared from the dibromide, palmitolic acid ($C_{16}H_{28}O_2$) by the action of alcoholic potash on the dibromide and gaidic acid by the action of nitrous acid on the hypogaecic acid. Gaidic acid is

¹ Bodenstein, *loc. cit.*

an isomer and bears the same relation to hypogaecic acid that elaïdic acid does to oleic acid.

We have carried through both of these procedures without being able to detect even a trace of hypogaecic acid. Using the first method a precipitate weighing a few milligrams was obtained which should have been hypogaecic acid according to Gössmann. It melted, however, at 70°, proving it to consist of saturated acids, lignoceric, arachidic, and stearic. The second method yielded a small precipitate melting at 59°C., evidently a mixture of palmitic and stearic acids. Since the lead salt of hypogaecic acid is soluble in ether, hypogaecic acid if present should go with the unsaturated acids as prepared by the lead-salt—ether method. Ten cc. of ether was added to 30 g. of unsaturated acids and cooled in an ice bath until a precipitate was obtained which was removed by filtering with suction through a chilled funnel. After recrystallizing from alcohol it melted at 70°–71°. Using alcohol instead of ether we obtained the same result. All these experiments were repeated several times but hypogaecic acid could not be detected. We are convinced that the two samples used for this investigation do not contain hypogaecic acid.

Saturated Acids.—The saturated acids were separated from the oil by the lead-salt ether method and esterified with methyl alcohol.¹ The mixture of methyl esters was then subjected to fractional distillation under diminished pressure.

The data of the distillation of the saturated acid esters of the Spanish oil are given in Table II. A preliminary distillation was made using a 1-liter Claisen flask, making 5 fractions, which were designated by the letters A to E, and a residue. These preliminary fractions were redistilled from a 250-cc. Ladenburg flask according to the manner indicated in the table. Seven fractions and a small residue were obtained.

TABLE II.

PEANUT OIL.

(From Spanish Type Peanuts.)

Fractional Distillation *in Vacuo* of Methyl Esters of Saturated Acids.
(105.85 g. Esters Subjected to Distillation.)

Fraction.	Preliminary Distillation.		Weight, G.
	Temperature, C.	Pressure, mm.	
A.....	168–171	4	23.97
B.....	171–174	4	17.80
C.....	174–180	4–3.5	21.04
D.....	180–195	3.5	14.51
E.....	195–217	3.5	15.92
Residue.....	12.49

Total 105.73

¹ THIS JOURNAL, 42, 1200 (1920).

TABLE II.—(Continued.)

<i>Final distillation.</i>			
Fraction.	Temperature, C.	Pressure, mm.	Weight, G.
A and B added..... 1	161-163	3	22.85
C added..... 2	164-168	3	24.27
..... 3	169-175	3	16.98
D added..... 4	176-186	3	9.60
E added..... 5	186-204	3	7.85
Original residue..... 6	204-225	3	11.60
added..... 7	225-240	3	11.24
Residue.....	1.11
Total			105.50

The iodine numbers which are a measure of the contaminating unsaturated acids, and saponification values of the various fractions are given in Col. 2 and 3, Table III. Using these data the percentages of unsaturated acids in each fraction were calculated and the saponification values and mean molecular weights corrected accordingly.¹ The mean molecular weights of the saturated acid esters are given in Col. 6.

TABLE III.
PEANUT OIL.

(From Spanish type peanuts.)

Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated Acids

Fractions.	Iodine number.	Saponification value.	Mean molecular weight.	Esters of unsaturated acids. %	Mean molecular weight of esters of saturated acids.			
1.....	2.0	202.4	277.2	1.70	276.9			
2.....	3.9	200.2	280.2	3.32	279.7			
3.....	7.1	194.6	288.3	6.05	287.8			
4.....	7.6	183.2	306.2	6.48	307.1			
5.....	7.6	173.0	324.2	6.48	326.5			
6.....	2.5	159.0	352.8	2.13	354.2			
7.....	1.9	153.5	365.5	1.62	366.9			
Fractions.	Palmitic Acid.		Stearic Acid.		Arachidic Acid.		Lignoceric Acid	
	%.	G.	%.	G.	%.	G.	%.	G.
1.....	71.31	16.29	22.01	5.03
2.....	61.01	14.81	30.82	7.48
3.....	33.60	5.71	55.76	9.47
4.....	61.43	5.90	27.81	2.67
5.....	85.39	7.01	0.16	0.01
6.....	47.26	5.48	46.71	5.42
7.....	26.19	2.94	68.41	7.69
Residue ^a	1.07
Total	36.81	27.88	18.10	14.19

^a Assumed to be pure methyl lignocerate.

¹ THIS JOURNAL, 42, 152, 1197 (1920).

Inspection of these results indicates what acids may be present in the various fractions. The mean molecular weights of the saturated acid esters in Fractions 1 to 3 lie between the molecular weights of methyl palmitate (270.3) and methyl stearate (298.4), and indicate, therefore, mixtures of these two esters. Fraction 4 is evidently a mixture of methyl stearate and methyl arachidate (326.4). The molecular weights of Fractions 5 to 7 are consistent with the presence of behenic acid ester but it will be shown later that behenic acid is not present and there is left methyl arachidate and methyl lignocerate as the probable constituents of the last 3 fractions. In order to test the correctness of these deductions the free acids were recovered from the various fractions subjected to fractional crystallization from alcohol and the constituent acids identified by melting-point determinations and elementary analyses. The following acids were identified.

Lignoceric Acid, $C_{24}H_{48}O_2$, m. p. 80.5° .—From the residue an acid was isolated which melted at $80-80.5^\circ$. Elementary analysis gave the following results. Calculated for lignoceric acid: H, 13.13; C, 78.18. Found: H, 13.01; C, 78.14. From Fraction 7 an acid was obtained melting at 80° and having the following composition: H, 13.03; C, 78.03.

Arachidic Acid, $C_{22}H_{40}O_2$, m. p. 77° .—This acid was separated from the Fraction 7 mother liquor from the lignoceric acid crystallization. It melted at 76° and had the following composition. Calculated for arachidic acid: H, 12.91; C, 76.85. Found: H, 12.90; C, 77.05.

Stearic Acid, $C_{18}H_{36}O_2$, m. p. 69° .—The arachidic acid in Fraction 4 was crystallized out and stearic acid identified in the mother liquor by the melting point 67° and the following analytical data. Calculated for stearic acid: H, 12.76; C, 75.98. Found: H, 12.60; C, 75.95.

Palmitic Acid, $C_{16}H_{32}O_2$, m. p. 62.6° .—This acid was isolated from Fraction 1. The melting point was $62.5-63^\circ$ and the elementary composition was as follows. Calculated for palmitic acid: H, 12.59; C, 74.92. Found: H, 12.44; C, 74.87.

TABLE IV.
PEANUT OIL.

(From Virginia Type Peanuts.)

Fractional Distillation *in Vacuo* of Methyl Esters of Saturated Acids.
(115.9 g. Esters Subjected to Distillation.)

<i>Preliminary Distillation.</i>			
Fraction.	Temperature, $^\circ C.$	Pressure, mm.	Weight G.
A.....	182-183	7	23.16
B.....	183-188	7	21.90
C.....	188-195	7	21.32
D.....	195-215	7	18.54
E.....	215-229	7	12.74
F.....	220-230	5	11.29
G.....	230-245	5	5.20
Residue.....	1.65
Total			115.80

TABLE IV.—(Continued.)
Final Distillation.

Fraction.	Temperature, °C.	Pressure, mm.	Weight, G.
Fraction A and B..... 1 added	165-170	7	6.17
Fraction C added..... 2	170-175	7	43.38
Fraction D "..... 3	175-187	7	10.65
Fraction E "..... 4	188-198	7-5	14.37
Fraction F "..... 5	198-215	5-6	12.53
Fraction G "..... 6	215-240	6-5	12.06
..... 7	240-257	7-4	14.05
Residue.....	0.95
Original residue.....	1.65
Total			115.81

The distillation of the saturated acid esters of the Virginia oil was conducted similarly to the Spanish oil distillation. The data are given in Table IV. The analytical results obtained on the various fractions are set forth in Table V.

TABLE V.
PEANUT OIL.

(From Virginia Type Peanuts.)

Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated Acids

Fractions.	Iodine number.	Saponification value.	Mean molecular weight.	Esters of unsaturated acids. %	Mean molecular weight of esters of saturated acids.			
1.....	2.8	204.5	274.3	2.49	273.8			
2.....	3.6	201.9	277.9	3.20	277.3			
3.....	9.4	194.0	289.2	8.35	288.6			
4.....	11.6	187.5	299.2	10.30	299.5			
5.....	9.4	174.8	320.9	8.35	323.3			
6.....	2.9	161.8	346.7	2.58	348.2			
7.....	1.9	152.4	368.0	1.69	369.6			
Fractions.	Palmitic Acid.		Stearic Acid.		Arachidic Acid.		Lignoceric Acid.	
	%.	G.	%.	G.	%.	G.	%.	G.
1.....	80.94	4.99	11.58	0.71
2.....	68.93	29.90	22.97	9.96
3.....	30.31	3.23	56.88	6.06
4.....	82.13	11.80	3.38	0.49
5.....	9.67	1.21	78.00	9.77
6.....	57.00	6.87	36.47	4.40
7.....	21.64	3.04	72.93	10.25
Residue.....	1.51 ^a
Total	38.12		29.74		20.17		16.16	

^a This amount was crystallized from an alcoholic solution of the liberated acids of the residue.

Fraction 1 was cut small in order to test for myristic acid. The mean molecular weight of the saturated acid esters in the fraction (273.8) is greater than the molecular weight of methyl palmitate. This shows that this fraction contains the ester of palmitic and stearic acid and that myristic acid, or any other saturated acid with a molecular weight less than that of palmitic acid, is not present.

Tests For Behenic Acid, $C_{22}H_{44}O_2$.—If peanut oil contains behenic acid we should expect to find it in Fractions 6 and 7 of the Virginia oil distillation. According to the molecular weights, Fraction 6 contains methyl arachidate and either methyl behenate or methyl lignocerate, while Fraction 7 is composed of either methyl arachidate or methyl behenate and methyl lignocerate. So if we prove the presence of lignoceric acid in Fraction 6 and arachidic acid in Fraction 7 it is quite conclusive evidence that behenic acid is absent. Fractions 6 and 7 were each redistilled into three fractions which are designated as 61, 62, 63 and 71, 72, 73. If behenic acid is present it should be concentrated in Fractions 63 and 71. The free acids were recovered from Fractions 63 and the mean molecular weight was found to be 342.4. After recrystallizing several times from alcohol the molecular weight was 352.2. No behenic acid could be detected in the mother liquors. This shows that Fraction 63 was rich in lignoceric acid ester. Fraction 71 was subjected to similar treatment and found to consist of arachidic and lignoceric esters. As before noted Fraction 7 of the Spanish oil distillation was also found to consist of arachidic and lignoceric esters. Behenic acid therefore is not present.

TABLE VI.

PEANUT OIL.

(From Spanish Type Peanuts.)

Saturated Acids.

	G.	Percentage composition. %	Original oil. %	Glycerides in original oil. %
Palmitic.....	36.81	38.0	7.8	8.2
Stearic.....	27.88	28.7	5.9	6.2
Arachidic.....	18.10	18.7	3.9	4.0
Lignoceric.....	14.19	14.6	3.0	3.1
Total	96.98	100.0	20.6	21.5

Having now established the qualitative composition of the saturated acid it remains to calculate the quantitative composition. Using the mean molecular weight of the saturated acid esters as determined (Col. 6, Tables III and V) and the theoretical molecular weights of the two esters in each fraction, the percentages and amounts of the acids present in each fraction are calculated. Tables VI and VII give in Col. 2 the percentage composition of the saturated acids, in Col. 3 the percentages

of acids in the original oil and in Col. 4 the percentages of glycerides in the original oil.

TABLE VII.
PEANUT OIL.
(From Virginia Type Peanuts.)
Saturated Acids.

	G.	Percentage composition. %.	Original oil. %.	Glycerides in original oil. %.
Palmitic.....	38.12	36.6	6.0	6.3
Stearic.....	29.74	28.5	4.7	4.9
Arachidic.....	20.17	19.4	3.2	3.3
Lignoceric.....	16.16	15.5	2.5	2.6
Total	104.19	100.0	16.4	17.1

The percentage compositions of the saturated acids agree closely. Indeed the agreement is probably within the experimental error and it may be said that the saturated acids of these two oils have the same percentage composition. However, the Spanish oil contains 20.6 % of this saturated acid mixture while the Virginia oil contains only 16.4 %.

Summary.

A study has been made of the composition of two samples of peanut oil, one pressed from Spanish type peanuts grown in South Carolina, the other from Virginia type peanuts grown in Virginia.

The percentage composition of the saturated acids from the two oils is practically the same. But the oil from the Spanish type peanuts contains 20.6 % of this saturated acid mixture, while the oil from the Virginia type contains only 16.4 %.

The composition of these two oils was found to be as follows.

	Oil from Spanish type peanuts. %.	Oil from Virginia type peanuts. %.
Glycerides of { Oleic acid.....	52.9	60.6
{ Linolic acid.....	24.7	21.6
{ Palmitic acid.....	8.2	6.3
{ Stearic acid.....	6.2	4.9
{ Arachidic acid.....	4.0	3.3
{ Lignoceric acid.....	3.1	2.6
Unsaponifiable matter.....	0.2	0.3

Hypogaecic acid was carefully tested for, but could not be detected.