shaken and allowed to stand several days with occasional shaking. The clear supernatant liquid was next tested for excess of chloride or silver in a nephelometer and if a deficiency of either was found, a suitable amount of a 0.01 *N* solution of silver nitrate or potassium chloride was added and the shaking and testing were repeated. The process was continued until the amounts of chloride and silver were equivalent.

The weight of silver has been corrected to vacuum by subtracting 0.031 mg. per gram of metal. The atomic weights of silver and chlorine were assumed to be 107.880 and 35.457 respectively.

In the table the fractions are numbered in the order in which the bulbs were filled. In Analysis 1 the solutions were considerably more concentrated than 0.1 *N* when precipitation was carried out. The apparent effect of this was the occlusion by the precipitate of some of the chloride which slowly leached out, so that the end-point was not finally reached for some weeks. If this leaching out was not complete it would account for the somewhat higher result of this experiment. On the whole, however, the different fractions show no positive evidence of dissimilarity.

Number of analysis.	Fraction of $SiCl_4$.	Weight of $SiCl_4$ in vacuum. Grams.	Weight of silver in vacuum. Grams.	Weight of silver added in solution. Gram.	Corrected weight of silver in vacuum. Grams.	Ratio $SiCl_4$: 4 Ag.	Atomic weight of silicon.
1	12	10.43530	26.47403	0.02120	26.49523	0.393856	28.129
2	3	5.97853	15.17909	0.00395	15.18304	0.393764	28.089
3	9	8.79053	22.31981	0.00150	22.32131	0.393814	28.112
4	6	6.83524	17.35557	0.00060	17.35617	0.393828	28.114
					Average,	0.393815	28.111

While we wish to emphasize the fact we do not consider the evidence presented as final, it seems to indicate that the atomic weight of silicon is not far from 28.1 instead of the value 28.3 as now accepted by the International Committee on Atomic Weights.

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[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY OF THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE CHEMICAL COMPOSITION OF COTTONSEED OIL.

BY GEORGE S. JAMIESON AND WALTER F. BAUGHMAN.

Received February 14, 1920.

Although cottonseed oil has been an important article of commerce for a great many years, neither its qualitative nor quantitative chemical composition has been definitely established. Investigators agree that palmitic acid is the predominating saturated acid but the presence of stearic and arachidic acids has been asserted and denied. Hehner and Mitchell[1] found 3.3% of stearic acid in cottonseed oil stearine. Meyer[2]

[1] Hehner and Mitchell, *Analyst*, 21, 328 (1896).

[2] Meyer, *Chem. Ztg.*, 31, 793 (1907).

fractionally distilled *in vacuo* the methyl esters of the insoluble acids and then separated the saturated and unsaturated acids in the 2 highest boiling fractions by the lead salt ether method. By fractional crystallization from alcohol he obtained from the saturated acid portion a small quantity of an acid melting at 63–73° which he believed to be a mixture of stearic acid and arachidic acid. Lewkowitsch[1] states that "recent investigations by the author have shown that it is doubtful whether stearic acid does occur in cottonseed oil," and also that "small quantities of arachidic acid appear to be present."

Our knowledge of the composition of the unsaturated acids is not so uncertain. Hazura[2] after demonstrating the absence of linolenic acid and the presence of linolic and oleic acids, calculated the proportions of linolic and oleic acids from the observed iodine value of the unsaturated acids (143.0) and the theoretical values for linolic and oleic acids (181.4 and 90.0). He gave the approximate composition of the unsaturated acid as 60% linolic and 40% oleic. However, Lewkowitsch[1] gives the results of Farnsteiner, who found by direct experiment only 23.9% of linolic acid in the unsaturated acids. The calculated iodine value of a mixture of 23.9% linolic acid and 76.1% oleic acid is only 112.

In view of these conflicting statements in regard to the composition of cottonseed oil, it was thought well worth while to investigate this problem again.

The oil used in this investigation was cold pressed from one bushel of Sea Island cottonseed by means of an oil expeller. The lead salt ether method showed that it contained 23.0% of saturated acids and 72.5% of unsaturated acids. The iodine value (Hanus) of the unsaturated acids was 142.2, the saponification value 199.4 and the mean molecular weight, 281.3.

Examination of Unsaturated Acids.—Refined oil was used for the preparation of the unsaturated acids in order to obtain them uncontaminated with mucilaginous material, etc.

The bromine addition derivatives were prepared according to the method of Eibner and Muggenthalor[3] which is briefly as follows.

To the acids dissolved in dry ether and cooled to —10°, bromine is added slowly, after which the mixture is allowed to stand for 2 hours at —10°. Hexabromide, the bromo derivative of linolenic acid, is insoluble in ether. No precipitate insoluble in ether was obtained, which confirms the observations of previous investigators that cottonseed oil contains no linolenic acid. The excess of bromine was removed from the

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[1] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., **2**, 197.

[2] Hazura, *Z. angew. Chem.*, **1888**, 315.

[3] Lewkowitsch, *ibid.*, **1**, 573.

ethereal solution by washing it in a separatory funnel with an aqueous solution of thiosulfate. After removing all traces of water from the washed ether solution, the ether was removed by distillation and the residue boiled with 250 cc. of petroleum ether. The petroleum ether solution was allowed to stand in the ice box overnight and then the linolic tetrabromide was removed by filtering through a weighed Gooch crucible. The filtrate was reduced to about half its original volume by distillation, cooled again in the ice box and a second crop of tetrabromide crystals obtained which was likewise removed by filtration through a Gooch crucible. The filtrate was then 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. Linolic tetrabromide contains 53.33% of bromine, and oleic dibromide 36.18%, and it is a simple matter to calculate algebraically the proportion of tetrabromide and dibromide in the residue if we know the per cent. of bromine present.

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

	G.
Sample of unsaturated acids	2.6058
Linolic tetrabromide insoluble in petroleum ether, m. p. 113–114°	1.7619
Residue (dibromide and tetrabromide)	3.1298
Bromine content of residue	43.11%
Dibromide in residue 59.59% or	1.8650
Tetrabromide in residue 40.41% or	1.2648
Total tetrabromide found	3.0267
Linolic acid equivalent to tetrabromide 1.4124 g. or	54.20%
Oleic acid equivalent to dibromide 1.1899 g. or	45.66%

The percentages of linolic and oleic acids in the unsaturated acids are converted into percentages of glycerides in the original oil as follows:

	Found. %.	Calculated to bases of 100%. %.	Original oil. %.	Glycerides in original oil. %.
Oleic acid	45.66	45.72	33.15	34.64
Linolic acid	54.20	54.28	39.35	41.13
Total	99.86	100.00	72.50	75.77

A duplicate experiment gave 45.84% oleic acid and 54.16% linolic acid. The theoretical iodine value of a mixture consisting of 45.72% of oleic acid and 54.28% of linolic acid is 139.6, which agrees fairly well with the observed iodine value of the unsaturated acids (142.2).

In this connection it may be well to point out that the low results obtained for linolic acids when this method has been used by other investigators, not only for the examination of cottonseed oil but also for other oils, is due to the fact that they have considered the tetrabromide that crystallized out from the petroleum ether solution to represent the entire amount of linolic acid present, but it has been the experience of the authors that a considerable amount remains in solution with the dibromide. This is no doubt due to the formation of an isomeric liquid tetrabromide soluble in petroleum ether and melting at 57–58° as pointed out by Rollet,[1] Matthes and Boltze[2] and Takahashi.[3] Thus it is necessary to determine the bromine content of the residue left after evaporating off the petroleum ether and to calculate the proportions of tetrabromide and dibromide present.

Examination of the Saturated Acids.—The saturated acids were prepared from the crude oil by the lead salt ether method and esterified by dissolving in absolute methyl alcohol, saturating the resulting solution with dry hydrogen chloride and then heating under a reflux condenser for 15 hours. The ester layer was then separated from the alcohol layer, dissolved in ether and the solution washed first with water and finally with a dilute solution of sodium hydrogen carbonate. The ethereal solution was then dried with anhydrous sodium sulfate after which the ether was removed by distillation.

The mixture of methyl esters, which weighed 111 g. was subjected to fractional distillation under diminished pressure. The temperatures and pressures maintained during the distillation and the weights of the fractions are given in Table I. As indicated in the table, a preliminary

TABLE I.—COTTONSEED OIL.

Fractional Distillation *in vacuo* of Methyl Esters of Saturated Acids.

111 G. Esters Subjected to Distillation.

Fraction.		Temperature. °C.	Pressure. Mm.		Weight. G.
Preliminary distillation	1	170–171.5	6.5		23.50
	2	171.5–173	6.5		22.05
	3	173–174	7.0	6.5	23.55
	4	174–179	7.0	6.5	(22.85)[a]
	5	179–190	6.5		(11.90)[a]
Fraction 4 redistilled	6	165–170	5.5	4.0	20.45
Fraction 5 added to residue and distillation continued	7	167 quickly rose to 170 170–175	5.0	4.5	10.85
	8	175 quickly rose to 178 178–188	4.5		2.90
	9	181–191	4.5		2.80
Residue from preliminary distillation added to residue and distillation continued	10	191 quickly rose to 194 194–235	4.5		3.50
Residue					0.95
Total					110.55

[a] Not included in total.

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[1] Rollet, Hoppe-Seyler, *Z. physiol. Chem.*, 410, 421 (1909).

[2] Matthes and Boltze, *Arch. pharm.*, 250, 225 (1912).

[3] Takahashi, *C. A.*, 13, 1583 (1919).

distillation was made first, resulting in 5 fractions and a residue which remained in the distilling flask. Fraction 4 was then transferred to a smaller flask and redistilled. This distillate is designated as Fraction 6. Original Fraction 5 was then added to the residue in the small distilling flask and distilled into 2 fractions, numbers 7 and 8. The residue in the large distilling flask which remained after the preliminary distillation was then added to the residue in the small flask and distilled. Two fractions were collected, numbers 9 and 10, and a small residue remained in the flask. Thus the esters of the saturated acids were divided into 8 fractions and a residue.

The iodine numbers (per cent. of iodine absorbed) and the saponification values (mg. of potassium hydroxide required to saponify one g. of the esters) of the various fractions were determined with the results given in Cols. 2 and 3, Table II. The iodine numbers are a measure of the contaminating unsaturated acids[1] and it is possible to calculate the per cent. of esters of unsaturated acids in each fraction. Thus the iodine number of the free unsaturated acids is 142.2 from which we calculate the iodine number of the methyl esters of the unsaturated acids to be 135.4. The per cent. of esters of unsaturated acids in a fraction is given by the formula, $a \times 100/135.4$, in which a is the iodine value of the fraction. In Col. 5 and 6 of Table II are given the percentages and weights of unsaturated acid esters in each fraction.

TABLE II.—COTTONSEED OIL.

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

Fraction.	Iodine number.	Saponification value.	Mean molecular weight.	Unsaturated		Mean molecular weight of esters of saturated acids.	Myristic Acid.		Palmitic Acid.		Stearic Acid.		Arachidic Acid.	
				%.	G.		%.	G.	%.	G.	%.	G.	%.	G.
1	3.2	208.6	268.9	2.25	0.53	268.4	6.25	1.47	86.30	20.28	....	....	....	....
2	3.5	206.8	271.2	2.46	0.54	270.8	....	....	90.73	20.00	1.65	0.36	....	....
3	5.0	205.8	272.6	3.52	0.83	271.8	....	....	86.43	20.35	4.92	1.16	....	....
6	6.0	205.4	273.1	4.22	0.86	272.2	....	....	84.47	17.27	6.18	1.26	....	....
7	11.6	202.4	277.2	8.16	0.88	275.8	....	....	69.66	7.56	17.12	1.86	....	....
8	20.2	195.6	286.8	14.21	0.41	285.4	....	....	37.17	1.08	43.73	1.27	....	....
9	21.8	192.2	291.9	15.34	0.43	291.3	....	....	20.18	0.56	59.68	1.67	....	....
10	19.7	179.0	313.4	13.86	0.48	316.0	....	....	....	....	30.25	1.06	51.40	1.80
Residue:	21.6	170.9	329.2	15.19	0.14	335.3	....	....	....	....	....	....	80.44	0.76
Total					5.10			1.47		87.10		8.64		2.56

If we calculate the number of mg. of potassium hydroxide required to

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[1] It is not possible to effect a complete separation of the saturated and unsaturated acids by the lead salt ether method, and therefore the saturated acids so prepared are always contaminated by small amounts of unsaturated acids.

saponify the unsaturated acid esters in one g. of each fraction (per cent. of unsaturated acid esters multiplied by the saponification value of unsaturated acid esters (190.0)) and subtract from the saponification value of each fraction we have the number of mg. of potassium hydroxide required to saponify the saturated acid esters in one g. of each fraction. Dividing this by the per cent. of saturated acid esters in the fraction gives the saponification value of the saturated acid esters from which the mean molecular weight of the esters may be calculated, using 56.1 as the molecular weight of potassium hydroxide. This method of calculation has been more fully explained in a former paper.[1]

In Col. 7 are given the mean molecular weights of the methyl esters of the saturated acids in the various fractions. Inspection of these results indicates the possible saturated acid esters that may be present. The mean molecular weight of the saturated acid esters in Fraction 1 is 268.4, which is lower than methyl palmitate (270.3) and higher than methyl myristate (242.3), and suggests, therefore, that Fraction 1 contains a mixture of these 2 esters. The mean molecular weights of the saturated acid esters of Fractions 2–9, inclusive, lie between the values for methyl palmitate and methyl stearate (298.4), and indicate, therefore, mixtures of these 2 esters. The mean molecular weight of the saturated acid esters of Fraction 10 (316.0) indicates a mixture of methyl stearate and methyl arachidate (326.4). It will be observed that the value for the residue is somewhat higher than the molecular weight of methyl arachidate. However, the residue contained some products of decomposition, the effect of which is to lower the saponification value and raise the calculated mean molecular weight.

In order to test the correctness of these deductions, the next step in the investigation was to isolate the acids from the various fractions and establish their identity by melting-point determinations and analyses. The free acids were recovered and fractionally crystallized from 95% alcohol until constant melting points were obtained. The following acids were identified:

Arachidic Acid, $C_{20}H_{40}O_2$, m. p. 77°.—From the residue an acid was obtained melting between 76° and 77°. Elementary analysis[2] gave the following results:

Calc. for arachidic acid: H, 12.91; C, 76.85. Found: H, 12.92; C, 76.72

No other saturated acid could be detected in the residue.

From Fraction 10 there was obtained an acid melting at 76–76.5° which gave the following results on analysis.[2]

Found: H, 12.98; C, 76.93.

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[1] THIS JOURNAL, 42, 152 (1920).

[2] Analysis by Chas. E. F. Gersdorff.

Stearic Acid, $C_{18}H_{36}O_2$, m. p. 69°.—The Fraction 10 mother liquor from the arachidic acid crystallization was concentrated and an acid obtained melting at 68–69°. Upon analysis[1] the following results were obtained:

Calc. for stearic acid: H, 12.76; C, 75.98. Found: H, 12.85; C, 76.03.

Palmitic Acid, $C_{16}H_{32}O_2$, m. p. 62.6°.—From Fractions 2 and 3 large quantities of an acid melting at 62.5° were readily isolated. This together with the boiling points of the fractions is sufficient proof of the identity of the acid.

Myristic Acid, $C_{14}H_{28}O_2$, m. p. 53.8°.—As before pointed out, the mean molecular weight of the saturated acid ester of Fraction 1 (268.4) is lower than methyl palmitate, which suggests the presence of the ester of the next lower acid of the series, methyl myristate. In order to obtain a fraction richer in methyl myristate, that part of Fraction 1 which remained after taking out the portions for saponification value and iodine number determinations was redistilled *in vacuo* and 2 fractions collected as indicated below.

Fraction.	Pressure. Mm.	Temperature. ° C.	Weight of fraction. G.	Mean molecular weight.
a	13	186–187	8.2	265.0
b	13 8	187–188 176–178	15.3	269.6

It will be noted that the mean molecular weight of Fraction *a* is lower and of Fraction *b* higher than that of the original Fraction 1.

Fraction *a* was again redistilled at a pressure of 4.5 mm. and 2 fractions *a'* and *a''* collected. The free acids, recovered from the lower boiling fraction *a'* (weight 2.4 g.) were subjected to fractional crystallization from 95% alcohol. A fraction was obtained having a melting point of 53.5–54.0° which was not changed by further crystallization. The fraction was not large enough for an elementary analysis. However, the evidence at hand proves quite conclusively that it was myristic acid.

It is now established that the saturated acid esters in Fraction 1 are methyl myristate and methyl palmitate while Fractions 2–9, inclusive, contain methyl palmitate and methyl stearate. Fraction 10 contains methyl stearate and methyl arachidate and the residue methyl arachidate. Using the mean molecular weight of the saturated acid esters and the theoretical molecular weights of the esters present in each fraction it is possible to calculate the percentages and amounts of the acids present in each fraction. This has been done with the results given in Cols. 8–15, Table II.

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[1] Analysis by Chas. E. F. Gersdorff.

TABLE III.—COTTONSEED OIL.
Composition of the Saturated Acids.

	G.	%.	Original oil. %.	Glycerides in original oil. %.
Myristic acid	1.47	1.40	0.32	0.34
Palmitic acid	87.10	83.06	19.10	20.04
Stearic acid	8.64	8.24	1.90	1.98
Arachidic acid	2.56	2.44	0.56	0.58
Oleic acid	5.10	4.86	0.51	0.53
Linolic acid			0.61	0.64
Total	104.87	100.00	23.00	24.11

Table III gives, in Col. 2, the percentage composition of the saturated acids, in Col. 3, the percentages present in the original oil, and in Col. 4, the percentages of glycerides in the original oil.

Summary.

A study has been made of the composition of a sample of cottonseed oil, the results of which are given below:

COMPOSITION OF COTTONSEED OIL.

		%.
Glycerides of	Myristic acid	0.3
	Palmitic acid	20.0
	Stearic acid	2.0
	Arachidic acid	0.6
	Oleic acid	35.2
	Linolic acid	41.7
	Total	99.8

WASHINGTON, D. C.

[CONTRIBUTION FROM THE ESSENTIAL OILS LABORATORY, DRUG DIVISION, BUREAU OF CHEMISTRY.]

THE COMPOSITION OF OIL OF CHENOPODIUM FROM VARIOUS SOURCES.

BY E. K. NELSON.

Received February 28, 1920.

Since the oil of chenopodium, or American wormseed, has become the standard remedy for hookworm disease, the demand for it has increased considerably. In the producing region, Carroll county, Maryland, there are at least 7 distilling plants in operation during the season.

During October, 1919, authentic samples were collected by the author from 5 of these distilling plants, for the purpose of studying the variations in the product.

As pointed out by Schimmel and Co.,[1] the distillation of chenopodium

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[1] Report of Schimmel and Co., April, 1908.