

*Analysis.* Subs., 0.1065: HgS, 0.0903. Calc. for  $C_2H_5O_2Hg$ : Hg, 73.03. Found: 73.05.

### Summary

1. The substance prepared and described by Otto was not pure methylmercuric acetate.
2. Pure methylmercuric acetate has been prepared by four different methods.
3. The parent base of the methylmercuric salts has been isolated.
4. Methylmercuric acetate is found to be one of the products formed by the thermal decomposition of mercurous acetate in an atmosphere of nitrogen.

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[CONTRIBUTIONS FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE]

## THE CHEMICAL COMPOSITION OF SOYA BEAN OIL

BY WALTER F. BAUGHMAN AND GEORGE S. JAMIESON

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Soya bean oil is reported by Matthes and Dahle<sup>1</sup> to contain palmitic acid 15%, oleic acid 56%, linolic acid 19%, and linolenic acid 4.8%. This is obviously not correct because the theoretical iodine number of such a mixture is 98.1, while the iodine number of soya bean oil is about 130. Keimatsu<sup>2</sup> examined a sample which he found contained about 12% of saturated acids and about 80% of unsaturated acids. He reports the saturated acid fraction consists of palmitic and stearic acids and the unsaturated acid fraction contains about 50% of an isomer of linolic acid, yielding a tetrabromide melting at 158°, about 15% of ordinary linolic acid and about 35% of oleic acid. W. B. Smith<sup>3</sup> made an investigation of the composition of the unsaturated acids but not of the saturated acids. As a result he expresses the opinion that a soya bean oil having an iodine number of 134 contains approximately 2 to 3% of linolenic acid, 55 to 57% of linolic acid, 25 to 27% of oleic acid and 9 to 10% of saturated acids. The calculated iodine number of such a mixture agrees very well with that of the oil.

### Experimental

The oil used in this investigation was expressed in this Laboratory from

<sup>1</sup> Matthes and Dahle, *Arch. Pharm.*, **249**, 424 (1911).

<sup>2</sup> Keimatsu, *Chem.-Ztg.*, **35**, 839 (1911).

<sup>3</sup> Smith, *J. Ind. Eng. Chem.*, **14**, 530 (1922).

the mammoth yellow variety of soya beans by means of an oil expeller.

The important chemical and physical characteristics are given in Table I. The percentages of saturated and unsaturated acids were determined by the lead-salt-ether method and corrections were made for the small quantity of unsaturated acids, that is, precipitated and weighed with the saturated acid fraction.<sup>4</sup> The percentage of unsaturated acids has also been corrected for the unsaponifiable matter that remains with the unsaturated acid fraction.

TABLE I  
SOYA BEAN OIL  
Physical and Chemical Characteristics

Specific gravity 25°/25°.....	0.9203	Unsaponifiable matter, %.....	0.6
Refractive index 20°.....	1.4736	Sat. acids (determined) %.....	12.7
Iodine number (Hanus).....	128.0	Unsat. acids + unsaponifiable matter (determined) %.....	83.0
Saponification value.....	189.5	Sat. acids (corrected) %.....	11.5
Acid value.....	0.5	Unsat. acids (corrected) %.....	83.5
Acetyl value.....	17.0	Iodine number of unsat. acids....	148.7
Reichert Meissl number.....	0.16	$\alpha$ -Iodine number.....	14.5
Polenske number.....	0.26		

**Unsaturated Acids.**—The bromine addition derivatives<sup>5</sup> were prepared and separated as follows.

A portion of the unsaturated acid fraction was dissolved in about 4 times its weight of absolute ether in a weighed centrifuge tube. This solution was cooled to about 0° and kept at this temperature while bromine was added at the rate of 1 or 2 drops per second until a deep red color was produced. The tube was allowed to remain over-night in a cold storage room at about 0° and then whirled in a centrifuge, which caused the precipitate to form a hard deposit on the bottom of the tube. The ether solution was decanted and the precipitate was washed 3 or 4 times with cold (0°) absolute ether. For each washing the precipitate was triturated in the ether with a glass rod and then centrifuged. After completing the washing the last traces of ether were removed by warming the tube to a temperature of about 50° in a vacuum oven and the precipitate of hexabromide was weighed. The ethereal solution and the washings were combined and washed in a separatory funnel with an aqueous solution of thiosulfate to remove the bromine. The solution was then dried with anhydrous sodium sulfate and the ether was removed by evaporation. The residue was boiled with sufficient petroleum ether to dissolve the greater part of it and placed in the ice box over-night. The precipitate, which consisted of tetrabromide and a small amount of hexabromide, was removed by filtering through a Gooch crucible, washed with petroleum ether, weighed and then dissolved in hot chloroform. This solution was collected in a weighed centrifuge tube. The chloroform was evaporated and the residue was treated with absolute ether which had been saturated with hexabromide at 0°. Practically all the residue went into solution and the tube was kept at 0° over-night. The tube was then centrifuged, the ether solution was decanted and the precipitate was washed as described above with cold (0°) absolute ether saturated at 0° with hexabromide. In this way a second crop of hexabromide was obtained.

<sup>4</sup> THIS JOURNAL, 42, 2398 (1920). *Cotton Oil Press*, 6, 41 (1922).

<sup>5</sup> Lewkowitsch, "Chemical analysis of Oils, Fats and Waxes," Longmans Green and Co., 5th ed., vol. I, pp. 568-580.

From 4.8118 g. of this unsaturated acid fraction, a first crop of hexabromide was obtained which weighed 0.3157 g. and melted with blackening at 179°. The second crop weighed 0.0286 g. and melted with blackening at 174°. When these 2 crops were combined and recrystallized from carbon tetrachloride, the melting point was raised to 181° and no darkening was observed. This quantity (0.3443 g.) of hexabromide is equivalent to 0.1262 g. of linolenic acid. The unsaturated acid fraction, therefore, contains 2.6% of linolenic acid.

The precipitate of tetrabromide from the same aliquot containing the small amount of hexabromide weighed 2.2264 g. and melted at 111°. The melting point of true linolic tetrabromide is 114°. A second crop, obtained by evaporating some of the petroleum ether, weighed 0.5433 g. and melted at 112.5°. No tetrabromide melting at 158°, as mentioned by Keimatsu, could be detected.

Having determined the percentage of linolenic acid, it is possible to calculate the percentages of linolic and oleic acids from the iodine number of the unsaturated acid fraction, 148.7, and the theoretical iodine number of the 3 acids; 274.1 for linolenic acid, 181.4 for linolic acid, and 90.1 for oleic acid. In this way the percentage composition of the unsaturated acids, tabulated below, was calculated.

	Composition of unsat. acid fraction %	Unsat. acids in oil %	Glycerides of unsat. acids in oil %
Linolenic.....	2.6	2.2	2.3
Linolic.....	59.0	49.3	51.5
Oleic.....	38.4	32.0	33.4
	<u>100.0</u>	<u>83.5</u>	<u>87.2</u>

**Saturated Acids.**—A portion of the saturated acid fraction separated by the lead-salt-ether method was esterified with methyl alcohol,<sup>6</sup> and the mixture of methyl esters was fractionally distilled under diminished pressure. As indicated in Table II, a preliminary distillation from a 1-liter Claisen flask divided the mixture into 5 fractions and a residue. These preliminary fractions were redistilled and 7 fractions and a residue were obtained.

TABLE II  
SOYA BEAN OIL  
FRACTIONAL DISTILLATION OF METHYL ESTERS OF SATURATED ACIDS  
(103.4 g. subjected to distillation)

Fraction	Temperature ° C.	Pressure Mm.	Weight G.
A	172-173.5	7	23.23
B	173.5-178	6	21.80
C	178-180	6	23.52
D	180-185	6	17.13
E	185-195	6	12.38

<sup>6</sup> THIS JOURNAL, 42, 1200 (1920).

TABLE II (Continued)

	Fraction	Temperature °C.	Pressure Mm.	Weight G.
	Residue			5.28
Fraction A distilled	1	155-160	3	16.69
Fraction B and C added	2	160	3	22.11
Fraction D added	3	160-164	3	24.62
Fraction E added	4	163-168	3	14.89
Residue added	5	168-177	2.5	16.07
	6	177-195	2.5	4.12
	7	195-220	3	3.95
Residue				0.87
				<u>103.32</u>

The iodine numbers, which are a measure of the contaminating unsaturated acids and the saponification values of these fractions, are given in Cols. 2 and 3 of Table III. The percentage of unsaturated acid esters in each fraction was calculated from the iodine numbers of these fractions and from that of the unsaturated acid fraction<sup>7</sup> which was separated by the lead-salt-ether method. These data permit the calculation of the mean molecular weight of the saturated acid esters in each fraction (Col. 6).

TABLE III  
SOYA BEAN OIL

RESULTS OF ANALYSES OF FRACTIONS OBTAINED BY DISTILLING METHYL ESTERS OF SATURATED ACIDS

Fraction	Iodine number	Saponification value	Mean molec- ular weight	Esters of unsat. acids %	Mean molecular weight of esters of sat. acids			
1	2.4	203.9	275.1	1.69		274.7		
2	3.7	202.1	277.6	2.61		277.2		
3	4.7	201.2	278.8	3.32		278.3		
4	9.3	196.8	285.1	6.56		284.5		
5	13.5	190.3	294.8	9.53		294.8		
6	13.0	179.7	312.2	9.17		313.9		
7	11.0	167.5	334.9	7.76		338.8		
Fraction	Palmitic acid		Stearic acid		Arachidic acid		Lignoceric acid	
	%	G.	%	G.	%	G.	%	G.
1	78.62	13.12	13.67	2.28	....	..	...	..
2	69.66	15.40	22.79	5.04	...	..	...	..
3	65.58	16.15	26.23	6.46	...	..	...	..
4	43.83	6.53	45.00	6.70	...	..	...	..
5	10.99	1.77	75.18	12.08	...	..	...	..
6	...	...	38.65	1.59	48.12	1.98	...	..
7	...	...	...	...	68.76	2.72	19.63	0.78
Residue	...	...	...	...	...	0.65	...	0.13
		<u>52.97</u>		<u>34.15</u>		<u>5.35</u>		<u>0.91</u>

<sup>7</sup> THIS JOURNAL, 42, 152, 1197 (1920).

The results in Col. 6 indicate the acids that may be present in the various fractions. The mean molecular weights of the esters in Fractions 1 to 5 lie between the molecular weights of methyl palmitate, 270.3, and methyl stearate, 298.4, which indicates that these 5 fractions consist of mixtures of these 2 esters in various proportions, in addition to the unsaturated acid esters. The probable constituents of Fraction 6 are methyl stearate and methyl arachidate (326.4) and of Fraction 7, methyl arachidate and methyl lignocerate.

The free acids were recovered from some of these fractions and the residue, by saponifying with alcoholic potash and decomposing the resulting soap with hydrochloric acid. The following acids were isolated by fractional crystallization from alcohol.

**Lignoceric Acid,  $C_{24}H_{48}O_2$ .**—A quantity of this acid was isolated from the residue. It melted at 79–80° and was analyzed with the following results.<sup>8</sup>

*Analysis.* Calc. for lignoceric acid: H, 13.13; C, 78.18. Found: H, 13.11; C, 78.29.

A quantity was also obtained from Fraction 7. It melted at 80° and had the following composition: H, 13.11; C, 78.32.

**Arachidic Acid,  $C_{20}H_{40}O_2$ .**—This acid was separated from the residue mother liquor from the lignoceric crystallization and identified by the melting point, 77°, and the following analytical data.

*Analysis.* Calc. for arachidic acid: H, 12.91; C, 76.84. Found: H, 13.01; C, 76.80.

It was also found in the Fraction 7 mother liquor from the lignoceric acid crystallization. This crop melted at 76–77° and had the following composition: H, 13.04; C, 76.80. Also from Fraction 6 a crop of crystals was obtained which melted at 76°.

**Stearic Acid,  $C_{18}H_{36}O_2$ .**—A quantity was isolated from Fraction 5. It melted at 69°.

*Analysis.* Calc. for stearic acid: H, 12.76; C, 75.98. Found: H, 12.88; C, 75.90.

**Palmitic Acid,  $C_{16}H_{32}O_2$ .**—The presence of this acid in Fraction 1 was proved by obtaining a crop of crystals which melted at 63°.

*Analysis.* Calc. for palmitic acid: H, 12.59; C, 74.92. Found: H, 12.47; C, 74.95.

This establishes the qualitative composition of the various fractions. The quantitative composition is calculated from the mean molecular weight of the saturated esters (Col. 6, Table III), and the theoretical molecular weights of the 2 saturated esters in each fraction. The proportion and amount of acids present in each fraction are given in Cols. 7 to 14, Table III.

The percentage composition of the saturated acid fraction is given in Col. 2 of Table IV, the percentages of acids in the original oil in Col. 3, and the equivalent percentages of glycerides in Col. 4.

<sup>8</sup> All elementary analyses were made by Chas. E. F. Gersdorff, of the Protein Investigation Laboratory.

TABLE IV  
SOYA BEAN OIL  
SATURATED ACIDS

Acid	Amounts	Composition	Acids in	Glycerides
	distilled	of sat.	original	in original
	G.	%	oil	oil
			%	%
Palmitic.....	52.97	56.73	6.5	6.8
Stearic.....	34.15	36.57	4.2	4.4
Arachidic.....	5.35	5.73	0.7	0.7
Lignoceric.....	0.91	0.97	0.1	0.1
	<u>93.38</u>	<u>100.00</u>	<u>11.5</u>	<u>12.0</u>

### Summary

The chemical composition of soya bean oil has been determined with the following results.

	Acid	%
Glycerides of	Linolenic.....	2.3
	Linolic.....	51.5
	Oleic.....	33.4
	Palmitic.....	6.8
	Stearic.....	4.4
	Arachidic.....	0.7
	Lignoceric.....	0.1
	Unsataponifiable matter.....	0.6

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[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE]

## THE CHEMICAL COMPOSITION OF SUNFLOWER-SEED OIL

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Sunflower-seed oil has been of commercial importance in Russia, Hungary, India and China for many years. In Russia it is used for culinary purposes, as a salad oil, and in making butter substitutes, soaps and Russian varnishes. It is stated that in 1911 more than 500 mills in the Caucasus were engaged in pressing sunflower seed and that some of the oil was exported to English refineries.<sup>1</sup> It is reported that this oil is used in the manufacture of the excellent Holland enamels.<sup>2</sup> Sunflower seed is grown in the United States, principally for poultry feed. In 1920, approximately six and one-half million pounds were produced in southeastern Missouri, southern Illinois and the San Joaquin Valley, California. This proved to be an overproduction for the feed trade and an effort was made to market the surplus to the oil mills. Owing to severe depression in the vegetable

<sup>1</sup> Bailey and Reuter, *U. S. Dept. Agr. Bull.*, 679 (1919).

<sup>2</sup> *Oil, Paint and Drug Rep.*, 98, No. 19, 49 (1920).