TABLE IV

SOYA BEAN OIL

SATURATED ACIDS

| Acid | Amounts distilled | Composition of sat. acid fraction | Acids in original oil | Glycerides in original oil |
|---|---|---|---|---|
| | G. | % | % | % |
| 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 |
| | 93.38 | 100.00 | 11.5 | 12.0 |

## 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 |
| | Unsaponifiable matter | 0.6 |

WASHINGTON, D. C.

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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

BY GEORGE S. JAMIESON AND WALTER F. BAUGHMAN

Received August 28, 1922

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.[1] It is reported that this oil is used in the manufacture of the excellent Holland enamels.[2] 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

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[1] Bailey and Reuter, *U. S. Dept. Agr. Bull.*, **679** (1919).

[2] *Oil, Paint and Drug Rep.*, **98,** No. 19, 49 (1920).

oil market at that time, however, the price offered was not satisfactory and the effort was not very successful. The following year the production declined to approximately 3,000,000 pounds. A demand for the seed at a satisfactory price as an oil producer would result in a greatly increased production.

Sunflower seed contains from 27 to 30% of oil. The hulls constitute from 46 to 49% of the seeds, so that by removing the hulls prior to pressing, a material very rich in oil is obtained. The press cake is a valuable stock feed, and has been used for many years in Europe.

Very little information in regard to the composition of the oil is reported in the literature. Lewkowitsch[3] states that the unsaturated acids consist chiefly of linolic acid, oleic acid being present only in small quantities, and Mitchell[4] expresses the opinion that linolenic acid is also present.

The oil used in this investigation was pressed from seed grown in southeastern Missouri. It had a pale yellow color, a mild taste and a pleasant odor.

**Physical and Chemical Characteristics.**—The more important characteristics are given in Table I. The high iodine number entitles it to be classified as a drying oil. It dries somewhat more slowly than soya bean oil.[5] The percentages of saturated and unsaturated acids were determined by the lead-salt–ether method and corrections were made for the small amount of unsaturated acids that contaminates and is weighed with the saturated acid fraction.[6] The percentage of unsaturated acids has also been corrected for the unsaponifiable matter, all of which separates with the unsaturated acid fraction. The iodine number of the unsaponifiable matter is 124.8 and of the unsaturated acid fraction, which contains the

TABLE I

SUNFLOWER-SEED OIL. PHYSICAL AND CHEMICAL CHARACTERISTICS

| | | | |
|---|---|---|---|
| Specific gravity, 25°/25° | 0.9193 | Sat. acids (determined) % | 7.4 |
| Refractive index, 20° | 1.4736 | Iodine number of sat. acid fraction | 5.0 |
| Acid value | 2.3 | Unsat. acids plus unsaponifiable matter (determined) % | 87.5 |
| Iodine number (Hanus) | 130.8 | Iodine number of unsat. acids plus unsaponifiable matter | 147.5 |
| Saponification value | 188.0 | Iodine number of unsat. acids | 147.9 |
| Acetyl value | 14.5 | Saturated acids (corrected) % | 7.1 |
| Reichert-Meissl number | 0.27 | Unsaturated acids (corrected) % | 86.6 |
| Polenske number | 0.25 | | |
| Unsaponifiable matter % | 1.20 | | |
| Iodine number of unsaponifiable matter | 124.8 | | |

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[3] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," MacMillan and Co., 5th ed., vol. **2**, p. 135 (1914).

[4] Mitchell, "Edible Oils and Fats," Longmans, Green and Co., **1918**, p. 70.

[5] For drying tests, see Henry A. Gardner, *Paint Mfrs.' Assoc. U. S., Bull.*, **53**, (1917) and *Circ.*, **136** (1921).

[6] THIS JOURNAL, **42**, 2398 (1920); *Cotton Oil Press*, **6**, 1, 41, May (1922).

unsaponifiable matter, 147.5. The iodine number of the pure unsaturated acids, therefore, is calculated to be 147.9.

**Unsaturated Acids.**—The bromine addition derivatives of the unsaturated acids were prepared.[7] No hexabromide was obtained, which indicates that linolenic acid is absent, but a large quantity of linolic tetrabromide, m. p. 114.0°, was obtained. Using the iodine number of the unsaturated acids (147.9) and the theoretical iodine numbers of linolic acid (181.4) and oleic acid (90.1), the percentages of linolic and oleic acids in the unsaturated acid fraction were calculated to be 63.3% of linolic acid and 36.7% of oleic acid, or 57.5% of linolic acid glyceride and 33.4% of oleic acid glyceride in the original oil.

**Saturated Acids.**—A quantity of the saturated acids, separated by the lead-salt–ether method, was esterified with methyl alcohol.[8] The mixture of methyl esters was fractionally distilled under diminished pressure. The data for this distillation are given in Table II. By a preliminary distillation from a 1-liter Claisen flask the mixture was divided into 5 fractions, designated by the letters A to E, and a residue. These preliminary fractions were redistilled from a 250cc. Ladenburg flask according to the manner indicated in the table, and 8 fractions and a residue were obtained.

TABLE II

SUNFLOWER-SEED OIL. FRACTIONAL DISTILLATION OF METHYL ESTERS OF SATURATED ACIDS

(114.3 g. subjected to distillation)

| | Fraction | Temperature ° C. | Pressure Mm. | Weight G. |
|---|---|---|---|---|
| | A | 168–169 | 5 | 23.18 |
| | B | 169–171 | 5 | 22.70 |
| | C | 171–175 | 5 | 23.50 |
| | D | 175–181 | 4.5 | 13.20 |
| | E | 181–198 | 4.5 | 15.72 |
| | Residue | | | 16.00 |
| | | | | 114.30 |
| Fractions A and B distilled | 1 | 163–164 | 5 | 7.28 |
| | 2 | 164–167 | 5 | 22.70 |
| Fraction C added | 3 | 167–172 | 5 | 23.00 |
| Fraction D added | 4 | 168–172 | 3.5 | 19.20 |
| Fraction E added | 5 | 172–182 | 3.5 | 18.10 |
| Residue added | 6 | 182–195 | 3.5 | 11.20 |
| | 7 | 195–219 | 3.5 | 8.90 |
| | 8 | 219–223 | 3.5 | 2.65 |
| | Residue | | | 1.10 |
| | | | | 114.13 |

The iodine numbers, which are a measure of the contaminating unsaturated acids and the saponification values of these fractions, are given in

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[7] Ref. 3, vol. **1,** pp. 568–578.

[8] THIS JOURNAL, **42,** 1200 (1920).

Cols. 2 and 3 of Table III. Using these data, the percentage of unsaturated acids in each fraction was calculated and the saponification values and mean molecular weights were corrected accordingly.[9] The mean molecular weights of the saturated acid esters are given in Col. 6.

TABLE III

SUNFLOWER-SEED OIL. RESULTS OF ANALYSES OF FRACTIONS OBTAINED BY DISTILLING METHYL ESTERS OF SATURATED ACIDS

| Fractions | Iodine no. | Saponification value | Mean molecular weight | Esters of unsaturated acids % | Mean molecular weight of esters of saturated acids |
|---|---|---|---|---|---|
| 1 | 4.0 | 205.5 | 273.0 | 2.84 | 272.5 |
| 2 | 4.0 | 203.3 | 275.9 | 2.84 | 275.4 |
| 3 | 7.3 | 200.8 | 279.4 | 5.18 | 278.6 |
| 4 | 11.8 | 195.9 | 286.4 | 8.37 | 285.4 |
| 5 | 18.4 | 189.7 | 295.7 | 13.06 | 295.7 |
| 6 | 15.7 | 183.1 | 306.1 | 11.14 | 307.7 |
| 7 | 4.5 | 161.5 | 347.4 | 3.19 | 349.5 |
| 8 | 7.1 | 157.7 | 355.7 | 5.04 | 359.6 |

| Fractions | Palmitic acid | | Stearic acid | | Arachidic acid | | Lignoceric acid | |
|---|---|---|---|---|---|---|---|---|
| | % | G. | % | G. | % | G. | % | G. |
| 1 | 84.91 | 6.18 | 7.25 | 0.53 | ... | .. | ... | .. |
| 2 | 75.41 | 17.12 | 16.81 | 3.82 | ... | .. | ... | .. |
| 3 | 63.35 | 14.57 | 26.70 | 6.14 | ... | .. | ... | .. |
| 4 | 40.19 | 7.72 | 46.94 | 9.01 | ... | .. | ... | .. |
| 5 | 7.92 | 1.43 | 74.90 | 13.56 | ... | .. | ... | .. |
| 6 | ... | ... | 56.57 | 6.33 | 28.24 | 3.16 | ... | .. |
| 7 | ... | ... | ... | ... | 54.50 | 4.86 | 38.41 | 3.42 |
| 8 | ... | ... | ... | ... | 37.10 | 0.98 | 54.14 | 1.43 |
| Residue | ... | ... | ... | ... | ... | .. | ... | 0.60[a] |
| | | 47.02 | | 39.39 | | 9.00 | | 5.45 |

[a] This amount was crystallized from an alcoholic solution of the free acids from the residue.

The results in Col. 6 indicate what acids may be present in the various fractions. The mean molecular weights of the saturated acid 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 these 2 esters in various proportions. The probable constituents of Fraction 6 are methyl stearate and methyl arachidate (326.4) and of Fractions 7 and 8, methyl arachidate and methyl lignocerate (382.5).

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. By fractional crystallization from alcohol, the following acids were isolated.

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[9] THIS JOURNAL, **42**, 152, 1197 (1920).

**Lignoceric Acid,** $C_{24}H_{48}O_2$.—The free acids recovered from the highly colored residue were dissolved in alcohol and treated with decolorizing carbon. After several crystallizations from alcohol, a fraction which melted at 81° was obtained.

*Analysis.*[10] Calc. for lignoceric acid: H, 13.13; C, 78.18. Found: H, 13.29; C, 78.17.

From Fraction 8, an acid was obtained which melted at 80°, and had the following composition: H, 13.03; C, 78.18.

**Arachidic Acid,** $C_{20}H_{40}O_2$.—This acid was separated from the mother liquor of Fraction 8 from the crystallization of lignoceric acid. It melted at 76–77°.

*Analysis.* Calc. for arachidic acid: H, 12.91; C, 76.85. Found: H, 12.98; C, 76.81.

Also from Fraction 7 an acid was obtained which melted at 77° and had the following composition: H, 12.93; C, 76.98.

**Stearic Acid,** $C_{18}H_{36}O_2$.—This acid was crystallized from Fraction 5 and identified by the melting point, 68–69°, and the following analytical data.

*Analysis.* Calc. for stearic acid: H, 12.76; C, 75.98. Found: H, 12.69; C, 76.10.

**Palmitic Acid,** $C_{16}H_{32}O_2$.—This acid was isolated from Fraction 1. The melting point, 63°, and the following analytical data identify it.

*Analysis.* Calc. for palmitic acid: H, 12.59; C, 74.92. Found: H, 12.62; C, 74.80.

The foregoing data establish the identity of the saturated acids in the various fractions and the residue. The quantities of the saturated acids present have been calculated from the mean molecular weights of the saturated acid esters (Col. 6, Table III) and the theoretical molecular weights of the 2 esters in each fraction. The results are given in Cols. 7 to 14, Table III.

TABLE IV

SUNFLOWER-SEED OIL. SATURATED ACIDS

| | Acids in sat. acid fraction | | Acids in original oil | Glycerides in original oil |
|---|---|---|---|---|
| | G. | % | % | % |
| Palmitic | 47.02 | 46.6 | 3.3 | 3.5 |
| Stearic | 39.39 | 39.1 | 2.8 | 2.9 |
| Arachidic | 9.00 | 8.9 | 0.6 | 0.6 |
| Lignoceric | 5.45 | 5.4 | 0.4 | 0.4 |
| | 100.86 | 100.0 | 7.1 | 7.4 |

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

## Summary

The chemical composition of sunflower-seed oil has been determined with the following results.

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[10] All elementary analyses were made by Chas. E. F. Gersdorff of the Protein Investigation Laboratory.

| | Acid | % |
|---|---|---|
| Glycerides of | Oleic | 33.4 |
| | Linolic | 57.5 |
| | Palmitic | 3.5 |
| | Stearic | 2.9 |
| | Arachidic | 0.6 |
| | Lignoceric | 0.4 |
| | Unsaponifiable matter | 1.2 |

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NO. 395]

# INFLUENCE OF SOME ORGANIC COMPOUNDS UPON THE HYDROLYSIS OF STARCH BY SALIVARY AND PANCREATIC AMYLASES

BY H. C. SHERMAN AND NELLIE M. NAYLOR

Received August 28, 1922

Various organic compounds have been reported as influencing the activity of amylases in the digestion of starch. In 1893[1] and again in 1904[2], Effront investigated the effects of certain amines and amino acids upon the hydrolysis of starches by an infusion of malt extract. Glycine, alanine, leucine, glutamic acid, hippuric acid, creatine, creatinine, asparagine and aspartic acid were found to increase the activity of the amylase, while amides and aliphatic amines appeared to act as inhibitory agents. Ford and Guthrie,[3] using Lintner soluble starch with malt extract and with a purified malt amylase, studied the effect of asparagine, glycine and alanine on the starch digestion. They ascribe the apparent increase of activity in the presence of the amino acids to the amphoteric property of these compounds or to their effect in neutralizing some inhibitory impurity in the starch or enzyme solution.

Terroine and Weill[4] tested the influence of many of the amino acids on the saccharification of starch by pancreatic juice. They report an activating influence on the part of the amino acids tested, but they make no statement regarding the hydrogen-ion concentration, or regarding the purity of any of the materials used.

Desgrez and Moog[5] report an activating influence exerted by methyl, ethyl and trimethyl amine hydrochlorides, on the hydrolysis of starch by a glycerol extract of dry pancreas. As in the work reported by previous investigators, there is no indication of any tests for hydrogen-ion concentration or for purity of materials used. Nor is there any evidence that

[1] Effront, *Mon. Sci.*, **41,** 266 (1893).

[2] Effront, *ibid.*, **61,** 561 (1904).

[3] Ford and Guthrie, *J. Chem. Soc.*, **89,** 76 (1906).

[4] Terroine and Weill, *Compt. rend. soc. biol.*, **72,** 542 (1912).

[5] Desgrez and Moog, *Compt. rend.*, **172,** 553 (1921).