

trated acid does and is therefore more convenient to handle although it takes more space.

The amount of cystine adsorbed by the Norite used in decolorizing the crude cystine was found to be small when the Norite had been boiled with dil. hydrochloric acid and filtered after decolorizing.

In determining the hydrogen-ion concentration of dark colored solutions a modification was made in the comparator used by Humitz, Meyer and Ostenberg.

The above investigation was suggested by Dr. H. C. Sherman. Appreciation is due also to Dr. A. W. Thomas and Dr. H. T. Beans for helpful advice.

NEW YORK CITY.

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

THE CHEMICAL COMPOSITION OF CORN OIL.

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Corn oil is produced from the germ of the corn kernel which is obtained by degerminating corn in the hominy, starch and glucose industries. The germ represents approximately 10% of the dry kernel and contains about 50% of oil. However, the commercially separated germs contain considerable portions from other parts of the corn which reduce the percentage of oil. About 75% of the corn oil output is used after refining for edible purposes. The poorer grades are used for soap making. It has also been used for the preparation of rubber substitutes.¹

Very little work on the composition of corn oil is reported in the literature. Lewkowitsch² states that the unsaturated acids consist of a mixture of oleic and linolic acids and quotes Vulte and Gibson as authority for the statement that the saturated acids consist of palmitic, stearic and arachidic acids. But Hehner and Mitchell³ could not detect stearic acid. Leathes⁴ states that hypogaecic acid occurs in corn oil.

The oil used in this investigation was pressed by means of an oil expeller from corn germs which had been produced by the so-called dry process.

Physical and Chemical Characteristics.—The more important physical and chemical characteristics are given in Table I. The saturated and unsaturated acids were determined by the lead-salt ether method.

¹ Sievers, "The Production and Utilization of Corn Oil in the United States," *U. S. Dept. Agriculture Bull.*, No. 904, 1920.

² Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan and Co., 5th ed. Vol. 2, p. 168.

³ Hehner and Mitchell, *Analyst*, 21, 328 (1896).

⁴ Leathes, "The Fats," Longmans, Green and Co., 1910, p. 15.

TABLE I.
 PHYSICAL AND CHEMICAL CHARACTERISTICS.

| | |
|--|-------------------|
| Specific gravity 25°/25° | 0.9185 |
| Refractive index 20° | 1.4717 |
| Iodine number (Hanus) | 117.2 |
| Saponification value | 187.3 |
| Unsaponifiable matter % | 1.7 ^a |
| Acid value | 2.5 |
| Acetyl value | 10.0 |
| Saturated acids (determined) % | 12.3 ^b |
| Unsaturated acids and unsaponifiable matter (determined) % | 83.3 |
| Saturated acids (corrected) % | 11.2 |
| Unsaturated acids (corrected) % | 82.5 |
| Iodine number of unsaturated acids and unsaponifiable matter | 136.9 |
| Iodine number of unsaturated acids | 137.2 |
| ^a Iodine number | 113.5 |
| ^b Iodine number | 12.3 |

Since a complete separation cannot be effected by this method, the percentages of saturated and unsaturated acids have been corrected for the small amount of unsaturated acids, as indicated by the iodine number of the saturated acid fraction, that contaminate and are weighed with the saturated-acid fraction.⁵ The content of unsaponifiable matter represents 1.7% of the oil which is about the average figure for corn oil. When separating the saturated and unsaturated acids by the lead-salt ether method the unsaponifiable matter goes with the unsaturated-acid fraction. Therefore the percentage of unsaturated acids has also been corrected for the unsaponifiable matter content of the unsaturated-acid fraction. The iodine number of the unsaponifiable matter is 113.5 and of the unsaturated-acid fraction containing the unsaponifiable matter, 136.9. The iodine number of the pure unsaturated acids is therefore calculated to be 137.2.

Unsaturated Acids.—The bromine addition derivatives of the unsaturated acids (and unsaponifiable matter) were prepared by dissolving a portion of the unsaturated-acid fraction, obtained by the lead-salt ether method, which contained 2% of unsaponifiable matter in absolute ether, cooling the solution to 10° and adding bromine slowly after which the solution was allowed to remain for 2 hours at a temperature of 10–15°.⁶ 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 and the residue dissolved in petroleum ether. This solution was allowed to remain overnight in the ice-box and then linolic tetrabromide which had crystallized was removed by filtration through a Gooch crucible.

⁵ THIS JOURNAL, 42, 11, 2398 (1920).

⁶ Lewkowitsch, Ref. 2, Vol. 1, p. 573.

The filtrate was reduced in volume, cooled in the ice-box and a second crop of tetrabromide crystals obtained and removed by filtration. The filtrate was evaporated to dryness, weighed, and the bromine content determined. This residue contained the oleic dibromide, the linolic tetrabromide that did not crystallize from the petroleum ether and the bromine derivative of the unsaponifiable matter. The iodine number of the unsaponifiable matter is 113.5 which is equivalent to a bromine number of 71.5. The bromine content of the brominated unsaponifiable matter is, therefore, 41.7%. From these data and the theoretical bromine contents of the linolic tetrabromide (53.33%) and oleic dibromide (36.18%) the percentages of tetrabromide and dibromide in the residue were calculated. The data of the analysis of the bromine derivatives are given below.

| | G. | %. |
|---|--------|------|
| Sample of unsaturated acids containing 2% unsaponifiable matter... | 3.1035 | |
| Linolic tetrabromide insoluble in petroleum ether, m. p. 114°..... | 2.0170 | |
| Residue (dibromide, tetrabromide and brominated unsaponifiable matter)..... | 3.7669 | |
| Brominated unsaponifiable matter in residue..... | 0.1065 | |
| Bromine content of residue..... | | 41.7 |
| Bromine content of mixture of oleic and linolic bromine derivatives..... | | 41.4 |
| Dibromide in mixture of oleic and linolic bromides..... | 2.5462 | 69.6 |
| Tetrabromide in mixture of oleic and linolic bromides..... | 1.1142 | 30.4 |
| Total tetrabromide..... | 3.1312 | |
| Linolic acid equivalent to tetrabromide..... | 1.4612 | 48.0 |
| Oleic acid equivalent to dibromide..... | 1.6245 | 53.4 |

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

| Acid. | Found. %. | Calculated to basis of 100%. %. | Original oil. %. | Glycerides in original oil. %. |
|---------|--------------|---------------------------------------|---------------------|--------------------------------------|
| Oleic | 53.4 | 52.7 | 43.4 | 45.4 |
| Linolic | 48.0 | 47.3 | 39.1 | 40.9 |
| Total | 101.4 | 100.0 | 82.5 | 86.3 |

The calculated iodine number of the unsaturated acid mixture having the percentage composition represented in Col. 2 is 133.3, while the determined iodine number of the unsaturated acids after correcting for the unsaponifiable matter is 137.2.

Test for hypogaecic acid, $C_{16}H_{30}O_7$.—This is an unsaturated acid whose melting point is 33–34°. It was tested for by a method similar to that used for testing peanut oil for hypogaecic acid.⁷ A 500g. portion of the unsaturated acid fraction was allowed to remain in a cold storage room where a temperature below 0° was maintained for several days. It had been completely solidified and was removed to another room where the temperature was slightly above 0°. After several days most of the

⁷ THIS JOURNAL, 43, 6, 1372 (1921).

mass had liquefied. The small amount of solid material that remained was removed by rapid filtration through a previously cooled Büchner funnel. It weighed about 10 mg. After crystallizing from 75% alcohol it melted at 61–62°. This melting point indicates that it consisted chiefly of palmitic acid with enough impurity (stearic acid) present to lower the melting point. It is believed that corn oil does not contain hypogaecic acid.

Saturated Acids.—A portion of saturated acids prepared by the lead salt-ether method was esterified with methyl alcohol.⁸ The mixture

TABLE II.
FRACTIONAL DISTILLATION OF METHYL ESTERS OF SATURATED ACIDS.
(97.0 g. Subjected to Distillation.)

| Fraction. | Temperature C. | Pressure. Mm. | Weight. G. |
|----------------------------|-------------------|------------------|---------------|
| A | 157 | 3 | 22.0 |
| B | 157–158 | 3 | 23.3 |
| C | 159–163 | 3 | 23.6 |
| D | 163–175 | 3 | 19.3 |
| E | 175–186 | 3 | 5.2 |
| Residue | | | 3.7 |
| | | | <hr/> 97.1 |
| Fraction A and B distilled | 1 | 153 | 2.5 |
| | 2 | 154–156 | 2.5 |
| Fraction C added | 3 | 156–159 | 2.5 |
| Fraction D added | 4 | 159–164 | 2.5 |
| Fraction E added | 5 | 164–173 | 2.0 |
| Residue added | 6 | 173–188 | 2.0 |
| | 7 | 188–215 | 2.0 |
| Residue | | | <hr/> .25 |
| | | | <hr/> 96.90 |

of methyl esters was then subjected to fractional distillation under diminished pressure. The data of the distillation are given in Table II. A preliminary distillation was made from a 1-liter Claisen flask, making 5 fractions which are designated by the letters A–E and a residue. The preliminary fractions were redistilled from a 250cc. Ladenburg flask according to the manner indicated in the table. Seven fractions and a residue were obtained.

The iodine numbers which are a measure of the contaminating unsaturated acids and the saponification values of the various fractions are given in Cols. 2 and 3, Table III. Using these data the percentage of unsaturated acids in each fraction was calculated and the saponification values and mean molecular weights corrected accordingly.⁹ The mean molecular weights of the saturated acid esters are given in Col. 6.

⁸ THIS JOURNAL, 42, 6, 1200 (1920).

⁹ *Ibid.*, 42, 152, 1197 (1920).

TABLE III.
RESULTS OF ANALYSES OF FRACTIONS OBTAINED BY DISTILLING METHYL ESTERS OF SATURATED ACIDS.

| Fraction: | Iodine number. | Saponification value. | Mean molecular weight. | Esters of unsaturated acids. %. | Mean molecular weight of esters of saturated acids. | | | |
|-----------|-------------------|-----------------------|------------------------|---------------------------------|---|-------|---------------------|-------|
| 1 | 2.5 | 204.5 | 274.3 | 1.91 | 273.9 | | | |
| 2 | 2.9 | 204.0 | 275.0 | 2.22 | 274.6 | | | |
| 3 | 4.5 | 202.9 | 276.5 | 3.44 | 275.8 | | | |
| 4 | 9.7 | 200.0 | 280.5 | 7.42 | 279.4 | | | |
| 5 | 17.0 | 193.1 | 290.5 | 13.00 | 289.8 | | | |
| 6 | 17.9 | 185.6 | 302.3 | 13.69 | 303.1 | | | |
| 7 | 11.9 | 165.0 | 340.0 | 9.10 | 345.0 | | | |
| Residue | | | | | | | | |
| Fraction. | Palmitic acid. %. | G. | Stearic acid. %. | acid. G. | Arachidic acid. %. | G. | Lignoceric acid. %. | G. |
| 1 | 81.09 | 6.28 | 11.98 | 0.93 | | | | |
| 2 | 78.53 | 17.36 | 14.26 | 3.15 | | | | |
| 3 | 73.64 | 17.60 | 18.01 | 4.31 | | | | |
| 4 | 59.36 | 12.39 | 28.57 | 5.96 | | | | |
| 5 | 25.24 | 3.05 | 57.55 | 6.95 | | | | |
| 9 | | | 69.03 | 4.17 | 13.28 | 0.80 | | |
| 7 | | | | | 58.15 | 2.27 | 29.04 | 1.13 |
| Residue | 56.68 | | 25.47 | | 3.07 | | 0.15 ^a | |
| | 56.68 | | 25.47 | | 3.07 | | 1.28 | |

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

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 1-5 lie between the molecular weights of methyl palmitate (270.3) and methyl stearate (298.4) and indicate mixtures of these two esters. Fraction 6 is probably a mixture of methyl stearate and methyl arachidate (326.4) while the molecular weight of Fraction 7 is consistent with the presence of behenic acid ester but this acid could not be detected when the free acids from this fraction were fractionally crystallized from alcohol so the probable constituents are methyl arachidate and methyl lignocerate (382.5).

In order to test the correctness of these deductions the free acids were recovered from some of the 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, $C_{24}H_{48}O_2$.—By fractionally crystallizing the free acids from Fraction 7 a fraction was obtained which melted at 79-80°.

Analysis. Calc. for lignoceric acid: H, 13.13; C, 78.18. Found:¹⁰ H, 13.21; C, 78.26.

¹⁰ Analyses by Chas. E. F. Gersdorff.

The free acid preparation obtained from the highly colored residue was dissolved in alcohol and treated with decolorizing carbon. The acid fraction crystallized from this solution weighed 0.15 g. and had a melting point of about 80°. After 4 recrystallizations the melting point was 80–80.5°. There was not sufficient material for an elementary analysis, but the melting point together with the presence of lignoceric acid in Fraction 7 is sufficient evidence to identify it as lignoceric acid.

Arachidic acid, $C_{20}H_{40}O_2$.—This acid was separated from the Fraction 7 mother liquor from the lignoceric acid crystallization. On one fraction which melted at 76–77° the following analytical results were obtained.

Analyses. Calc. for arachidic acid: H, 12.91; C, 76.85. Found:¹⁰ H, 13.22; C, 76.89. Another fraction which melted at 77° had the following composition:¹⁰ H, 13.07; C, 76.73.

Stearic Acid, $C_{18}H_{36}O_2$.—From Fraction 5 an acid was obtained which melted at 68–69°.

Analysis. Calc. for stearic acid: H, 12.76; C, 75.98. Found:¹⁰ H, 12.82; C, 76.05.

Palmitic acid, $C_{16}H_{32}O_2$.—This acid was isolated from Fraction 1. It melted at 62.5°.

Analysis. Calc. for palmitic acid: H, 12.59; C, 74.92. Found:¹⁰ H, 12.30; C, 74.73.

The qualitative composition of the saturated acids having been established the quantitative composition is calculated from the mean molecular weight of the saturated acid esters as determined (Col. 6, Table III) and the theoretical molecular weights of the two esters in each fraction. Thus the percentages and amounts of acids present in each fraction were calculated.

TABLE IV.
SATURATED ACIDS.

| | G. | Percentage composition. %. | Original. %. | Glycerides in original oil. %. |
|------------|-------|-------------------------------|-----------------|-----------------------------------|
| Palmitic | 56.68 | 65.6 | 7.3 | 7.7 |
| Stearic | 25.47 | 29.4 | 3.3 | 3.5 |
| Arachidic | 3.07 | 3.5 | 4 | .4 |
| Lignoceric | 1.28 | 1.5 | .2 | .2 |
| | 86.50 | 100.0 | 11.2 | 11.8 |

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

Summary.

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

| COMPOSITION OF CORN OIL. | | %. |
|--------------------------|-------|------|
| Glycerides of. | | |
| Oleic acid | | 45.4 |
| Linolic acid | | 40.9 |
| Palmitic acid | | 7.7 |

COMPOSITION OF CORN OIL (*continued*).

| Glycerides of. | %. |
|-----------------------------|-------------|
| Stearic acid | 3.5 |
| Arachidic acid | 0.4 |
| Lignoceric acid | 0.2 |
| Unsaponifiable matter | 1.7 |
| | <u>99.8</u> |

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NEW BOOKS.

Pyrometric Practice. Technologic Paper of the Bureau of Standards, No. 170. By PAUL D. FOOTE, C. O. FAIRCHILD, and T. R. HARRISON. Government Printing Office, Washington, D. C., 1921. 326 pp. 185 figs. 18 × 25.5 cm. Price \$0.60; from Supt. of Documents.

Only a few years ago the average investigator knew little of pyrometry. The whole subject was a vast mystery to him; he knew something of the use of a mercury thermometer, but a thermocouple, a resistance thermometer, or a radiation-pyrometer would not have been recognized by him, much less understood. To-day the chemist, as well as the physicist and the engineer, is obliged to make frequent and increasing use of one or more of the modern types of thermometer. In the laboratory some form of pyrometer is an indispensable tool; in the plant the size and importance of pyrometric installations has created a new profession, "pyrometric engineering."

This publication is a clear and thorough presentation of the technic of temperature measurement. The authors possess a first-hand knowledge of the subject, and have made frequent contributions to the various branches of pyrometry. The scope of the book is shown by the following list of chapter-headings: Temperature Scale; High-temperature Thermometry; Thermoelectric Pyrometry; General Theory of Optical and Radiation Pyrometry; Optical Pyrometry; Radiation Pyrometry; Resistance Thermometry; Recording Pyrometry; High Temperature Control; Melting-point Methods at High Temperatures; Standardization of Pyrometers; and Industrial Applications of Pyrometry.

As indicated by the title, the book is primarily concerned with the practical side of the subject. It contains "nothing of the historical, and the purely scientific aspects of pyrometry have been intentionally subordinated. It purports to describe practical methods in use in the industries in the year 1920." Nevertheless the theoretical foundations of the various phases of temperature-measurement are recorded, insofar as they are required for a proper understanding of the instruments and methods. While this treatise naturally will find its widest use in connection with industrial installations, it will be helpful to anyone who is called upon to measure temperatures. Of especial value to the research worker is the