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THE NATURE AND PROPERTIES OF CORN OIL.

II. DETERMINATION OF THE CONSTITUTION.

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IN the present investigation an attempt has been made to identify, so far as possible, the series of fatty acids contained in maize oil. Although a complete separation has not been effected, owing to the difficulty of isolating these acids and to the imperfect knowledge we have of their properties, it has been found practicable to determine the principal acids found in the oil, including three never before reported, and to definitely settle the relationship existing between maize oil and other oils possessing somewhat similar properties.

The oil of maize is a fixed seed oil, composed of a highly complex mixture of glycerides of the fatty acids, together with a small proportion of some volatile oil and a rather large percentage of unsaponifiable matter.

CONSTITUENTS OTHER THAN FATTY ACIDS.

The question of the nature of the volatile oil peculiar to corn oil has not been considered in the present article. Its existence has been recognized by nearly all observers, and it is to this cause that the characteristic grain-like odor and taste of the oil are due.

The unsaponifiable matter is very largely phytosterol or phytosteryl alcohol. The amount present, as determined by the process of Foster and Reichelmann, is found to be 1.41 per cent., a rather large amount in comparison with that in most seed oils. To the presence of phytosterol is due one of the most characteristic tests for maize oil ; *i. e.*, a fine violet coloration when one drop of concentrated sulphuric acid is added to a carbon disulphide solution of the oil and the mixture is allowed to stand for twenty-four hours.

A small amount of lecithin is also present in the unsaponifiable matter. The method of Benedikt and Lewkowitsch was employed for this determination and the amount of phosphorus pentoxide recovered was 0.98 per cent. From this, the calculated amount of lecithin present in maize oil is 1.11 per cent., making the total amount of unsaponifiable matter 2.52 per cent.

The percentage of glycerol, as determined by Hehner's dichromate method, is somewhat high, running from 10.35 to 10.55 per cent.

INSOLUBLE FATTY ACIDS.

The mixed insoluble fatty acids were prepared in considerable bulk, for analysis, by a process analogous to that used in determining the Reichert value, except that no attempt was made to have the work quantitative. The oil was saponified by aqueous potassium hydroxide in considerable excess, the soap decomposed by dilute sulphuric acid, and the resultant liquid heated until the oily layer of liberated fatty acids became clear and transparent. The whole mass was then transferred to a separating funnel, the aqueous layer drawn off, and the fatty acids washed with boiling water until the wash-water was neutral to litmus. The insoluble acids were then subjected to a steam distillation at the ordinary pressure and the residue washed with boiling water, filtered through a dry filter, and dried at 100° C. Considerable difficulty was found in obtaining uniform samples for analysis, owing to the sharp separation of the acids into a solid and a liquid portion.

The ordinary constants of the mixed insoluble acids, prepared as above, were first determined, the melting-point being established by the method of La Sueur and Crossley[1] and the saponification value both by titration and by the Koettstorfer method. A tabulation of the results obtained follows :

Sp. gr. at 100° C.	0.8529
Melting-point	22.4° C.
Iodine absorption	120.98
Bromine thermal value	21.6° C.
SAPONIFICATION VALUE.	
By titration	198.29
By Koettstorfer	200.01
MEAN COMBINING WEIGHT.	
By titration	282.98
By Koettstorfer	280.64

In connection with these results a statement is given of the figures obtained by other observers, as follows :

COMPARISON WITH RESULTS OF OTHER OBSERVERS.

MELTING-POINT.

Melting-point acids.	Observers.	References.
10.5°–12.2° C.	Hoppe-Seyler[2]	Bull. Soc. Chim. (1866),[2], **6**, 342.
16°–18° C.	Dulière	J. Pharm. (1897), 217.
18°–20° C.	DeNegri and Fabris	Ztschr. anal. Chem., **33**, 547.
20° C.	Jean	J. Soc. Chem. Ind., **11**, 504.
39.5° C.	DeNegri[3]	Chem. Ztg., **22**, 961–976.

IODINE ABSORPTION.

Hübl No. acids.	Observer.	Reference.
113–115	De Negri and Fabris	Ztschr. anal. Chem., **33**, 547.
123.27	De Negri[3]	Chem. Ztg., **22**, 961.
125	Spüller[2]	Dingl., **264**, 626.
126.4	Hopkins	J. Am. Chem. Soc., Dec., 1898.

SAPONIFICATION VALUE.

Sapon. value.	Mean. mol. wt.	Observer.	Reference.
198.4	282.76	Hart	Chem. Ztg., **6**, 1522.

An attempt was next made to obtain an approximate idea of the relative amounts of liquid and of solid fatty acids present in the mixture and, for this purpose, the method proposed by Muter and De Koningh[4] was employed. The results obtained must not be regarded as entirely accurate, since the lead salts of the acetic

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[1] *J. Soc. Chem. Ind.*, Nov. 30. 1898.

[2] Ether extract.

[3] Petroleum ether extract.

[4] Allen : "Commercial Organic Analysis," Vol. II(I), 247.

series of fatty acids are not wholly insoluble in ether and those of the oleic and the linolic series are not completely soluble. The constants of the two fractions were then determined, great care being taken to avoid oxidation during the process, and a tabulation of the results obtained follows :

	Percentage.	Iodine absorption.	Molecular weight.	Koettstorfer figure.
Liquid fatty acids....	72.26	135.97	284.45	197.22
Solid fatty acids......	27.74(calc.)	54.23	269.78	207.94

Wallenstein and Finck report an iodine absorption figure of 140.7 for the liquid fatty acids of this oil, a somewhat higher figure than has been obtained in the present investigation.

It will be noticed that the percentage of liquid fatty acids is high. The terms "liquid" and "solid" used in this connection are misleading since, as will be shown later, one of the principal acids of maize oil is both solid and unsaturated, having its lead salt soluble in ether.

FRACTIONAL PRECIPITATION OF MIXED ACIDS.

Forty grams of the mixed insoluble fatty acids were dissolved in hot neutral alcohol, care being taken to use enough alcohol to insure complete solution at all temperatures. To the hot liquid was added a boiling solution of 1.5 grams magnesium acetate in alcohol and the mixture was then thoroughly agitated and allowed to stand for twenty-four hours. As no precipitate was thrown down, the operation was repeated with a second portion of magnesium acetate and, upon standing, a white solid, like the scrapings of candles, separated out. This precipitate was filtered off and a fresh portion of magnesium acetate added to the filtrate as before, the operation being repeated as long as it was possible to obtain new precipitates. In this manner four successive fractions were separated, all white and all but the first curdy in appearance. The fifth fraction was obtained by making the liquid strongly alkaline with ammonia, before the addition of fresh magnesium acetate, and allowing the mixture to stand for three days before filtering. The sixth and seventh fractions were obtained by neutralizing the liquid with acetic acid and then treating it with lead acetate. The precipitate thus obtained was filtered off, dissolved in ether as far as possible, and the insoluble portion filtered out. The final fraction, having its lead salt soluble in ether, was then freed from the ether by gently heating the liquid.

The several fractions were next well washed with cold dilute alcohol, dried in filter-paper, and decomposed by hot, dilute hydrochloric acid. The liberated fatty acids were then washed with boiling water until neutral to methyl orange, filtered and dried as in the Hehner and Angell process. The purified acids were now examined for melting-point, iodine absorption, bromine absorption, saponification figure, and mean molecular weight.

In the determination of melting-point, a short piece of glass tubing with small bore was coated over one end with a film of the acid and bound to the bulb of a delicate thermometer. This was immersed in water, which was gradually raised in temperature. The point at which the fatty film was detached from the tube and rose to the surface was recorded as the melting-point.

A tabulation of the results obtained follows, and it will be observed that the acids constituting the several fractions give a pretty regular series of values for all constants determined.

APPEARANCE OF THE SEVERAL FRACTIONS.

1. White waxy mass like the scrapings of candles.
2. White warty substance like soft tallow.
3. Pale yellow solid, rather harder than butter.
4. Buttery, dark brown mass. The magnesium salt of this fraction was very stable and, upon being decomposed by acid, immediately oxidized to a dark brown color. The filtrate was colored bright yellow and had a peculiar odor, showing that some decomposition-product had been formed.
5. Similar to 4, but somewhat softer.
6. Similar to 1.
7. Dark red-brown liquid, of comparatively low viscosity.

	Melting-point.	Mean mol. weight.	Saponification value.	Iodine absorption.	Bromine absorption.	Equivalent iodine absorption.
1	50.2	272.00	206.25	15.35	....	....
2	37.2	276.03	203.24	69.74	....	....
3	35.8	284.76	197.00	101.94	64.55	102.46
4	31.1	289.75	193.62	102.77	66.23	105.14
5	21.5	287.60	195.06	114.98	73.22	116.26
6	55.2	268.11	209.24	9.51	5.32	8.45
7	Liquid	286.07	196.11	137.61	85.91	136.39

An examination of the several fractions and of their constants, as given in the foregoing table, indicates the presence, particularly in the fourth fraction, of some unsaturated fatty acid which is readily oxidizable in the air. The melting-point and iodine absorption of this fraction suggest hypogaeic acid, and an ultimate analysis of the substance, twice repeated, gave a formula very nearly corresponding to $C_{16}H_{30}O_2.2H_2O$, except that the percentage of oxygen was somewhat high. The presence of water, due to the impossibility of completely drying so oxidizable an acid, explains the high molecular weight of this fraction and the excess of oxygen is, of course, due to the oxidizability of the oil. From the foregoing evidence the presence of hypogaeic acid as a characteristic acid of maize oil may be considered as conclusively proved.

A separate investigation, in the method suggested by Renard,[1] was conducted to determine the presence of arachidic acid. A small crop of crystals was obtained, showing the characteristic form of arachidic acid under the microscope, but the quantity recovered was too small for further investigation.

The occurrence of stearic, palmitic, and oleic acids in maize oil was first reported by Hoppe-Seyler[2] in 1866. He succeeded in isolating these acids, and their presence has since been confirmed by many observers. Linolic acid was first determined in 1894 by Rokitiansky,[3] who prepared its oxidation-product, sativic or tetrahydroxystearic acid. This result is confirmed by a late observer, C. G. Hopkins,[4] of Cornell University, who finds a large percentage of linolic acid in corn oil. Rokitiansky also asserts the presence of a hydroxylated acid (probably ricinoleic) in the solid fatty acids, and this conclusion is rendered probable by the somewhat high acetyl figure (11.12–11.49) of the oil.

A summary of the insoluble fatty acids shown to exist in the oil of maize is therefore as follows:

Name of acid.	Formula.	Name of analyst.
Stearic	$C_{18}H_{36}O_2$	Hoppe-Seyler
Palmitic	$C_{16}H_{32}O_2$	Hoppe-Seyler
Arachidic	$C_{20}H_{40}O_2$	Vulté and Gibson
Hypogaeic	$C_{16}H_{30}O_2$	Vulté and Gibson
Oleic	$C_{18}H_{34}O_2$	Hoppe-Seyler
Linolic	$C_{18}H_{32}O_2$	Rokitiansky
Ricinoleic(?)	$C_{18}H_{34}O_3$	Rokitiansky

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[1] Allen: "Commercial Organic Analysis," II (I), 134.

[2] *Bull. Soc. Chim.* (1866), [2], 6, 342.

[3] *Ph. Russ.* (1894), 712–713.

[4] This Journal, 20, 948.

SOLUBLE FATTY ACIDS.

In the determination of the constants of maize oil, the Reichert value (4.2–4.3) obtained as the result of a large number of tests was found to be higher than that of any other seed oil, cocoanut oil (3.5–3.7) coming next. The figures obtained for this constant by other analysts differ widely in value, running from 0.0[1] to 6.7.[2] The Reichert value and high percentage of glycerine indicate the presence of a notable amount of volatile acids and, as comparatively little attention has been paid to their determination, certain observers going so far as to doubt their existence, it was thought well to attempt their identification, so far as possible. For this purpose the mixed acids were prepared as in the Hehner and Angell process, and the insoluble acids filtered off. An aliquot portion of the filtrate was then neutralized with decinormal potassium hydroxide, methyl orange indicator and the titration continued until neutral to phenolphthalein. The excess of decinormal potassium hydroxide of course represents the soluble fatty acids. (It was found that 1 gram of the oil required 0.0088 gram potassium hydroxide for the neutralization of its volatile acids, this corresponding to a Reichert value of 3.9 and a mean molecular weight of about 130.)

The larger part of the filtrate was then saturated with calcium chloride and allowed to stand. A small amount of oil separated out, showing the presence of acids higher than formic and acetic. but lower in the series than lauric. No attempt was made to identify the acids in this fraction, but Rokitiansky reports the probable presence of caproic, caprylic, and capric acids.

A portion of the aqueous liquid was carefully separated from all oily drops and heated with alcohol and concentrated sulphuric acid. The fragrant and characteristic odor of ethyl acetate was produced in a marked degree, thus establishing the presence of acetic acid, an acid never before reported for maize oil. As a confirmatory test, ferric nitrate was added drop by drop to a portion of the original filtrate. The blood-red color characteristic of ferric acetate was obtained and responded to the usual tests for establishing its identity.

Another portion of the original filtrate was treated with silver

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[1] Hopkins.

[2] Morse: N. H. Expt. Sta. Bull. (1892). **16**, 19.

nitrate and gently warmed. A marked precipitate of metallic silver was formed, this proving the presence of formic acid in corn oil. This acid was reported by Rokitiansky, but its occurrence has not been confirmed by any later observer.

The soluble acids thus far determined in corn oil are therefore summarized as follows:

Name of acid.	Formula.	Name of analyst.
Formic	CH_2O_2	Rokitiansky
Acetic	$C_2H_4O_2$	Vulté and Gibson
Caproic[1]	$C_6H_{12}O_2$	Rokitiansky
Caprylic[1]	$C_8H_{16}O_2$	Rokitiansky
Capric[1]	$C_{10}H_{20}O_2$	Rokitiansky

Scientific knowledge as to the properties of the various fatty acids is at present so scanty and fragmentary and the lack of any connected scheme for their analysis is so absolute that the complete investigation of any oil presents almost insurmountable difficulties. Further examination of corn oil is needed in order to establish or disprove the presence of caproic, caprylic, capric, and ricinoleic acids and also to determine the relative percentages of the various acids with accuracy. The present investigation adds to the known constituents of the oil, acetic, hypogaeic, and arachidic acids, and confirms the presence of formic acid, which was up to this time considered doubtful.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

KILGORE'S MODIFICATION OF THE VOLUMETRIC METHOD OF ESTIMATING PHOSPHORIC ACID.[2]

BY C. B. WILLIAMS.

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IN the laboratories of fertilizer control stations and other institutions where a large number of determinations of phosphoric acid are required to be made quickly and accurately each year, it has been recognized for some time as almost imperative that some method shorter than the "gravimetric" should be devised. In 1894 Mr. Kilgore, then reporter on phosphoric acid for the Association of Official Agricultural Chemists, realizing this

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[1] Probable only.

[2] Read before the November meeting of the North Carolina Section of the American Chemical Society.