The statistics given herewith present our estimate of the world's production of fatty raw materials brought down to the basis of actual oil produced from the oilseeds and plants, and show the importations into the principal consuming countries. They may be of interest and will give an idea of the great extent of this industry.

ESTIMATED WORLD'S PRODUCTION OF OILS AND FATS

Oil-bearing Seeds	31,500,000 Tons of 2240 lbs.
Available for crushing	22,750,000 Tons of 2240 lbs.
Oil produced after crushing	6,500,600 Tons of 2240 lbs.
Production of other oils and fats	2,086,000 Tons of 2240 lbs.
Total Available Supply of Oils and Fats	8,586,600 Tons of 2240 lbs.

The largest oilseed production in the world is Cottonseed, amounting to .... 9,325,000 Tons

The quantity of seed available for crushing would be about 8,000,000 tons, giving an oil equivalent of .... 1,440,000 Tons

Peanuts are the next largest crop, the world's production being given as .... 4,195,000 Tons

The quantity of seed available for crushing is 3,000,000 tons, giving an oil equivalent of .... 1,080,000 Tons

The importations of oil-bearing seeds, oils and fats into some of the largest consuming countries are as follows:

	Oilseeds	*Oils & Fats (In tons of 2240 pounds)*	*Total Equivalent as Oil*
U. S. A.	1,082,295	790,743	1,209,871
Germany	1,644,019	436,388	995,343
United Kingdom	1,623,292	453,861	932,736
France	1,432,840	96,174	637,166
Holland	725,630	170,737	408,887
Italy	417,154	76,186	228,894
Denmark	438,703	43,305	171,428

Does Margaric Acid Occur In Alfalfa Seed Oil

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THE statement that a fatty acid of an uneven number of of carbon atoms has been found in nature always arrests attention because if, indeed, this be actually the case, then current views on the mechanism of fatty acid formation in the living organism require revision.

In this connection a brief literature review might not be without interest. Chevreul, some 120 years ago, coined the word "margaric" to fit, appropriately, the fatty acid of seventeen carbon atoms which he had isolated from "margarin." Heintz[1] later dared to question the existence of such an acid. With Krafft's[2] successful synthesis of a straight-chain saturated fatty acid of the same properties as were reported by Chevreul for his margaric acid there was re-opened the question of the validity of the latter's findings. Gerard[3], apparently encouraged by the success previously claimed by others in isolating this acid from natural sources hopefully gave the name daturic to one of similar composition, and allegedly isomeric with it, recovered from the seed oil of Jimson weed, *Datura stramonium* L. Soon after the turn of the century Holde[4] in an attempt at confirmation of not only the latter's conclusions but also those of others with respect to palm oil[5] and pig fat[6], although failing in his objective yet succeeded, by judicious crystallization, in demonstrating that what had been described by them as a chemical individual was nothing but a mixture of stearic and palmitic acids.

A more recently reported, and still unchallenged, source of this acid is the seed oil of the alfalfa plant, *Medicago sativa* L. On searching the later literature, and particularly the standard reference books and treatises in the fatty oil field, it was found that the conclusions of Jacobsen and Holmes[7] are most often cited in substance in support of the view that the biochemical synthesis of the fatty acids is not necessarily limited to those of an even number of carbon atoms.

We, too, in an earlier investigation of this oil[8] on making a fractional distillation of the methyl esters of the saturated fatty acids had obtained data, calculated from saponification values, which raised the hope that a heptadecanoic acid had been found at last. Lack of material, however, for making confirmatory tests by the mixed melting point technic and desire to apply phase rule principles to the study made necessary the treatment of a larger quantity of oil than had been available before in order to insure an adequate supply of saturated acids of which there are present here *ca* 7 per cent[8]. To that end 100 pounds of seed which had been grown in Arizona, and described as "Registered Hairy Peruvian, 5-3 strain," was extracted with petroleum ether (38°-40°) which had been treated, in turn, with concentrated and fuming sulfuric acids, and then alkali solution. It had been dried over calcium chloride before distillation. Saturated acids were separated from the unsaturated by the method of Baughman and Jamieson[9]. Some 350 grams of solid acids were thus obtained. By several reprecipitations in the form of lead soaps followed by reconversion to the free acids, the iodine number of the mixture was lowered from an initial 17 to less than unity. Final purification was effected by replicated crystallizations from alcoholic solution. Some 225 grams of acids were finally available for esterification.[10] From this quantity there was obtained, after purification, *ca* 190 grams of methyl esters.

Distillation of the methyl esters was carried out *in vacuo* (1 mm.) in an all-glass apparatus fitted with a jacketed, electrically heated 15-inch Widmer column[11] and a four-receptacle receiver so adjusted as to obviate the necessity of breaking the vacuum when removing fractions. Pressures were manostatically controlled (±.03 mm.)[12] and distillations were made in a cottonseed oil bath which was internally heated with a resistance coil. Four fractions and the inevitable residue were obtained in the first fraction. In subsequent fractionations, a small Widmer column was used. Fractions most nearly alike in appearance, temperature of distillation, and molecular weight by saponification were combined and refractionated. The end in view was to obtain fractions corresponding in properties to the pure methyl esters of the C_{16}-C_{18} acids. That is, fractionation was continued until one was obtained of molecular weight 284, corresponding to that of the methyl ester of margaric acid. Those fractions lower than this value were recombined in an attempt to obtain one of molecular weight corresponding to the ester of palmitic acid, while from the higher fractions one comparable to the ester of stearic acid was sought. Seven fractionations (Table 1) were made before the desired three were obtained.

The problem was then narrowed to an investigation of the first three fractions, of primary importance being characterization of fraction A. On *a priori* grounds, two conclusions suggested themselves, viz: pure methyl margarate or for on an eutectic mixture of the palmitate and the stearate.

The palmitic and stearic acids used as controls in the mixed melting point determinations, although of high purity when purchased yet were several times crystallized from solution before use. Molecular weight and melting point of each agreed with the accepted values for these acids. Margaric acid was synthesized by adding carbon dioxide to the corresponding (cetyl alcohol) Grignard compound[13]. The purified product had the following characteristics: m.p. (corr.) 59.85°C.; molecular weight from saponification value 269.8 (theory 270.2). These acids were then converted into their methyl esters.

The determination of melting points when to fractions A, B, and C, respectively, there was added pure methyl stearate left much to be desired in that the evidence was not conclusive. No depression in melting point was observed in the case of fraction C. It was concluded, therefore, that this fraction was the pure stearate. On the other hand, the observed depressions in melting points of fraction A and B were so small that they were deemed to be of no significance, the mixture softening below its melting point with the result that the latter appeared to take place over a 0.2°-range. Melting points observed in the case of mixtures of all three fractions in turn with the palmitate and margarate exhibited the same inaccuracies. Because of this erratic behavior of the esters, a condition also observed by others[14], the application of mixed melting point analysis to the problem in hand appeared impractical. Attention, therefore, was centered upon the freezing point of each fraction as offering perhaps a better point of departure in the characterization thereof.

Shriner and colleagues[14] have determined the freezing points of the ternary system of palmitic, margaric and stearic acids. Their work was repeated for the two-fold purpose of determining with what exactness their results are reproducible and of checking the purity of the acids used as reference materials in this study. It was found that in all cases the freezing points checked with 0.1° of their values and that calculations of the percentage composition of a mixture of palmitic and stearic acids from the observed freezing point gave results within one unit of the theoretical value of the mixture.

Each fraction was hydrolyzed for the purpose of recovering its fatty acids, after which they were purified by recrystallization from alcohol. The mean molecular weight (M) of each was determined. The treatment given each acid fraction follows. To pure stearic acid (f.p., 68.5°) there was added an approximately equimolecular weight of fraction C (M 284.8). The freezing point of the mixture was found to be 68.6°. Increasing the relative proportions of unknown to known acid (3 to 1) produced no further change. This fraction was obviously stearic acid. When acid fraction B (M 255.6) was mixed in varying proportions with pure palmitic acid (f.p., 60.7°), a freezing point of 60.65° was observed, an indication of the fact that palmitic acid alone constituted this fraction.

Acid fraction A (M 270.8) received the following treatment. Freezing point determinations were made of four mixtures of pure stearic acid containing varying amounts of this fraction. Each mixture was then calculated into molar-percent composition of stearic and margaric acids, and the alternative one of stearic and palmitic on the assumption that the fraction in hand consisted of an equimolecular mixture of these acids (Table 2). From the composition and observed freezing point data a graph was plotted (Figure 1). Since each of the four points fell directly on the curve for the palmitic-stearic acid system as developed by Shriner et al[14], it appears that this fraction does not consist of margaric acid, but that it is an equimolecular mixture of the foregoing acids.

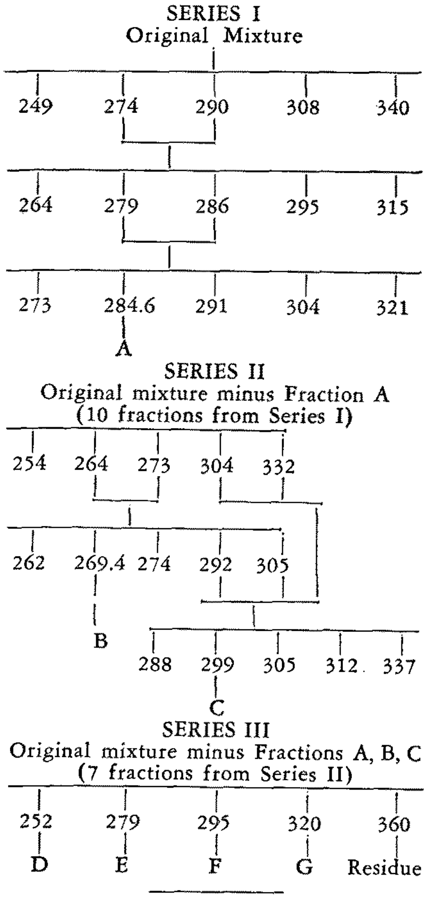
Fractions E and F were treated in the same manner as was fraction A. In both cases all points obtained fell on the palmitic-stearic acid curve. Since the mean molecular weights of the remaining fractions (D and G) were such as to indicate the presence of an acid lower than palmitic and higher than stearic acid, respectively, these two fractions were not similarly treated because of a lack of reference data. The observed freezing point of fraction D (52.3°) suggests the presence here of myristic acid along with palmitic; that of fraction G (74.6°) suggests a mixture of stearic and arachidic, or even a higher homolog.

TABLE I.
Refractionation of Methyl Esters of Saturated Fatty Acids
(Mean molecular weights only recorded)

Fraction	Molecular weight	Weight g.	Apparent Composition pct.
A	284.6	25.6	margaric, 100
B	269.4	24.7	palmitate, 100
C	299.0	22.3	stearate, 100
D	252.0	20.2	myristate, 65; palmitate, 35
E	279.0	17.0	palmitate, 68; stearate, 32
F	295.0	14.0	palmitate, 10; stearate, 90
G	320.0	8.2	stearate plus higher homolog
Residue	....	......	(too badly charred for study)

TABLE 2
Freezing Points of Mixtures of Acid Fraction A and Stearic Acid.

Mixture	Composition (alternative) mol-pct	F.p. calc'd. °C.	F.p. obs'd. °C.
1	0.490 C_{17} + 0.510 C_{18}	61.5	
	0.245 C_{16} + 0.755 C_{18}	62.6	
			62.55
2	0.670 C_{17} + 0.330 C_{18}	60.05	
	0.330 C_{16} + 0.670 C_{18}	60.30	
			60.35
3	0.750 C_{17} + 0.250 C_{18}	59.60	
	0.375 C_{16} + 0.625 C_{18}	58.85	
			58.80
4	0.856 C_{17} + 0.144 C_{18}	59.30	
	0.428 C_{16} + 0.572 C_{18}	57.30	
			57.25



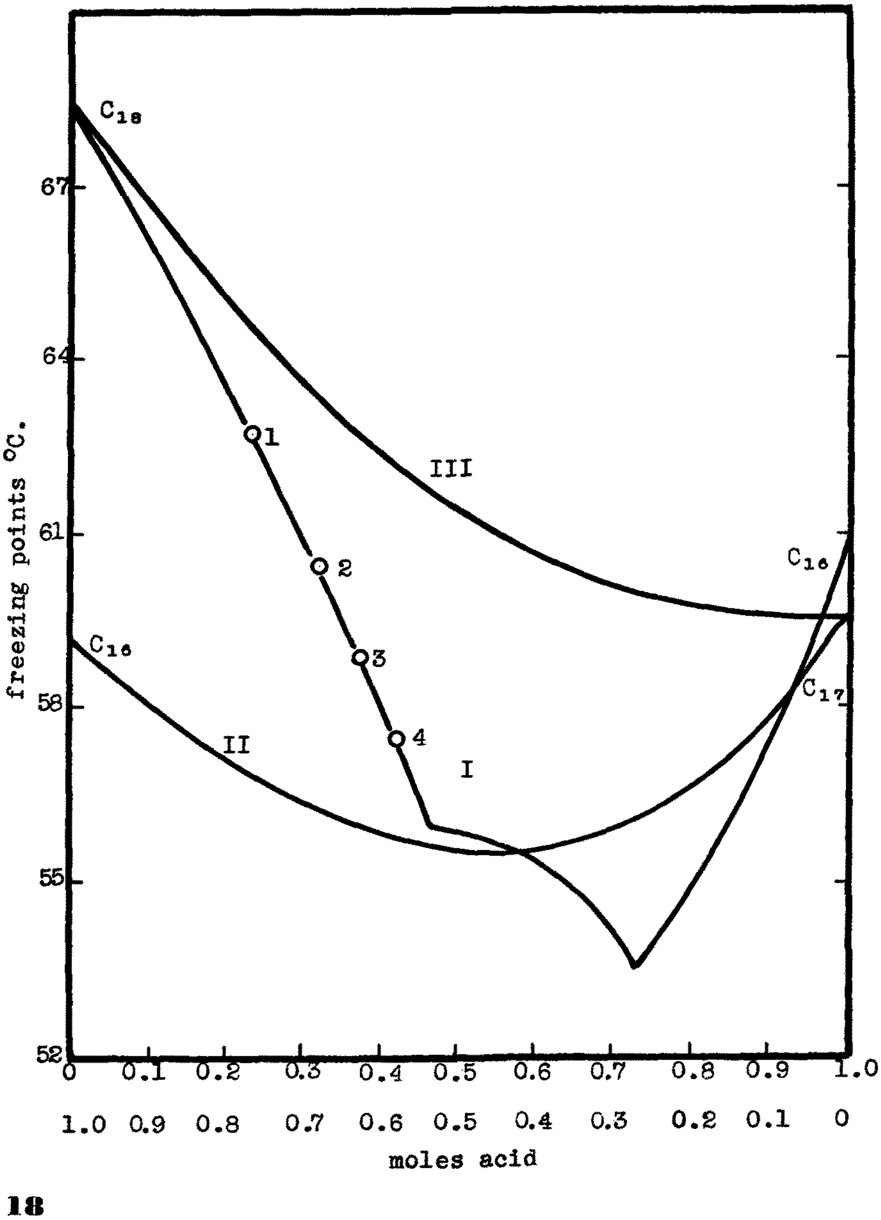


Figure 1
Freezing Points of Mixtures of Acid Fraction A and Stearic Acid (1-4) Compared with the Binary Freezing Point Curves Palmitic-Stearic (I), Palmitic-Margaric (II), and Margaric-Stearic (III) Acids of Shriner, Fulton and Burks (1933).

SUMMARY

The saturated fatty acids of alfalfa seed oil were investigated with the purpose of discovering whether or not the reported existence of a heptadecanoic acid here could be substantiated. By the application of phase rule principles to the analysis of a fraction which constituted approximately 6.3 per cent of the oil, it was found that this fraction was in reality not margaric acid but an equimolecular mixture of palmitic and stearic acids. The presence of these two acids in alfalfa seed oil has not been previously reported. Indications of the presence of myristic acid and higher homolog(s) of stearic acid have been found, although conclusive proof is wanting.

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1938 Report of the Glycerin Analysis Committee American Oil Chemists' Society

FOR approximately forty years the compound $(C_3H_6O_3Cu\ Na)_2.3H_2O$ has been known as the reaction product of cupric hydroxide, sodium hydroxide and glycerol in alcohol water solution(1). Various attempts have been made to utilize the solubility of this compound in a method for glycerol estimation, but until the publication of Bertram and Rutgers(2) no claim of success for such methods has been advanced.

In brief, Bertram and Rutgers Method consists in treating not more than 800 mg. glycerol in aqueous solution not exceeding 10 ml. volume, in a stoppered 100 ml. measuring flask, with 10 ml. 30% (w/v) NaOH, followed by 60 ml. EtOH (methylated spirit of 96-97% by vol. containing 5% MeOH may be used). After mixing, enough 10% (w/v) $CuCl_2.2\ H_2O$ alcoholic solution is added gradually, in small portions with thorough shaking, to produce a clearly visible, permanently undissolved precipitate of cupric hydroxide, after which the flask is filled to the mark with alcohol.

All of these operations are conducted at room temperature (20° C.). The well-mixed contents of the flask is centrifuged at about 1300 r.p.m. for 10 minutes, 50 ml. of the clear solution are pipetted into a 300 ml. Erlenmeyer flask and then are added in succession 100 ml. distilled water, 4.5N H_2SO_4 until a slightly acid reaction is obtained and then about 10 gms. KI. The mixture is titrated with O.1 N thiosulfate until a perfectly white color is obtained. 1 ml. O.1 N thiosulfate = 0.0001 mol. glycerol. A blank determination is made and subtracted from the sample titration. The value of the blank titration is quite constant and is due to the slight solubility of cupric hydroxide in the medium.

Bertram and Rutgers claim that this method may be adapted to the estimation of certain other hydroxylated compounds which must contain at least two hydroxyl groups in adjacent and favorable positions and must be soluble in dilute aqueous or alcoholic NaOH. From these considerations, as well as by experimental evidence, it may be seen that trimethylene glycol will not react but that some interference may be expected from polyglycerol ethers. NH_4 salts and sulfites interfere but are easily eliminated.

With the full realization that this method offers more potential advantages than any suggested in recent years, your committee decided to subject it to careful investigation. Although Bertram and Rutgers advise against the use of pure glycerol as a standard for the reason that "in the course of the purification process decomposition, condensation and polymerization to a slight extent may occur," it was thought advisable to test the method in a preliminary way upon a laboratory redistilled glycerol which, by commonly accepted standards, might be regarded as pure. As in previous years, a C. P. glycerin made from choice salt crude, was fractionated through an efficient column, under about 5 mm. pressure, the first and last portions, of about one-third each, being rejected and the middle portion, of constant boiling point, being accepted as of sufficient purity for our purpose. Before distribution to the committee this fraction was diluted to about 90% concentration in order to minimize weighing errors due to the excessively hygroscopic nature of pure glycerol. Members of the committee were provided with photostatic copies of Bertram and Rutgers' paper and requested to test the method in their own way upon this C. P. redistilled glycerin and on any other samples or by any other methods of appraisal deemed suitable.

The results of our tests so far indicate that the proposed procedure is more of a principle than a method of analysis. The average glycerol content of the redistilled sample, determined by pyknometer specific gravity and the Bosart and Snoddy table, is 89.31%. The average of all reported results on this sample by the Bertram Method is 88.32% based upon 43 actual determinations, with extreme variations ranging from 80.03 to 92.50%. Analyses made upon other distilled glycerin and upon a number of samples of crude glycerin show a similar divergence from accepted glycerol content obtained by specific gravity on distilled samples and analyses by the acetin method on crudes. A few trials were made upon refined natural oils, which may be regarded as practically pure triglycerides and are recommended by Bertram and Rutgers as standards. The glycerin yield of these samples showed much better agreement with the accepted value calculated from ester value, or determined by bichromate or pyridine-acetin analysis(3), though in several cases the deviation was considerably outside usual tolerances.

Members of the committee noted conflicts with the claims of Bertram