

exposed to its action, which in turn depends upon the degree of subdivision of the seed being extracted.

2. The properties of the pigment glands have been utilized for the development of a method for mechanically fractionating cottonseed into pigment glands, embryo tissue (meal), and hull tissue. The process consists in the treatment of finely divided cottonseed with mixtures of inert liquids having densities intermediate between those of the seed parts being separated.

3. The fractionation method has been shown to be applicable to the preparation of pigment glands, and pigment-free oil and meal from flaked cottonseed.

4. The method has also been shown to be applicable to the separation of pigment glands from defatted cottonseed.

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Selective Hydrogenation in the Preparation of Purified Oleic Acid From Animal Fats. Elimination of Extremely Low Crystallization Temperatures¹

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IN recent publications from this laboratory procedures for the preparation of purified oleic acid (oleic acid content, more than 90%) from red oil (commercial oleic acid) (1) and tallow (2) were described. The presence of appreciable quantities of polyunsaturated acids in these starting materials necessitated crystallization of the oleic acid from a solvent at extremely low temperatures (-50° to -60° C.), with attendant loss of product. Although crystallization at these low temperatures is probably feasible on an industrial scale, a purification procedure employing temperatures not lower than -20° C. would be less costly and would not require especially elaborate and expensive processing equipment.

If inexpensive mixtures of fatty acids consisting only of oleic, stearic, and palmitic acids, with oleic acid predominating, were available from natural sources, purified oleic acid could be prepared by the relatively simple process of eliminating the saturated acids by solvent crystallization at temperatures between -20° and 0° C. Crystallization of the oleic acid itself would not be required. Unfortunately no such desirable mixture of fatty acids is available from natural sources. It was the purpose of the present investigation to prepare by a simple method from readily available and inexpensive starting materials a mixture of fatty acids which would simulate the hypo-

thetical mixture referred to above and to determine the conditions required to give the best yield of high-purity oleic acid from such a mixture.

The fatty acids required were obtained from selectively hydrogenated inedible animal fats, such as the tallows and greases. Hydrogenation of triglycerides is a well-developed process, and it is possible to reduce the polyunsaturate content of a fat to a low level without appreciably hydrogenating the glycerides of oleic acid. This is illustrated in Table 1, which shows the effect of selective hydrogenation on the fatty acid composition of some typical animal and vegetable fats. When animal fats are hydrogenated under proper conditions, the fatty acids obtained by hydrolysis consist almost exclusively of oleic, palmitic and stearic acids, with only small proportions of isomeric oleic acids and minor quantities of polyunsaturated acids. This is in decided contrast to the vegetable oils, in which selective hydrogenation produces relatively large proportions of isomeric oleic acids. Hydrogenation of the animal fats at 150° C. under a hydrogen pressure of 10 to 15 pounds per square inch and with 0.1% nickel catalyst, is satisfactory.

In the work covered by this report the fatty acids from selectively hydrogenated Brown Grease (Table 1) were employed. The content of polyunsaturated acids was somewhat higher than that of other samples which we have processed, but this material was available in large quantities, and it was satisfactory for the purpose of illustrating the separations involved.

¹ Part of this paper was presented at the meeting of the American Oil Chemists' Society held in Chicago on October 27, 1944.

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TABLE 1
Effect of Selective Hydrogenation on Fatty Acid Composition of
Some Typical Animal and Vegetable Fats

| | Before Hydrogenation | | | | | After Hydrogenation | | | | |
|-----------------------------------|----------------------|----------|--------------------------------|--------------|--------------------|---------------------|----------|--------------------------------|--------------|--------------------|
| | Iodine Number | Oleic, % | Isomeric Oleic, ^a % | Saturates, % | Polyunsaturates, % | Iodine Number | Oleic, % | Isomeric Oleic, ^a % | Saturates, % | Polyunsaturates, % |
| Inedible tallow..... | 59.9 ^b | 51.6 | 1.6 | 40.7 | 6.1 ^c | 49.5 ^b | 46.0 | 4.8 | 47.1 | 2.1 ^c |
| Brown Grease..... | 51.8 ^b | 45.6 | 2.5 | 48.0 | 3.9 ^c | 41.7 ^b | 40.8 | 4.0 | 54.4 | 0.8 ^c |
| Cottonseed oil ^d | 103.0 | 27.1 | | 26.9 | 46.0 | 55.4 | 43.6 | 16.7 | 37.7 | 2.0 |
| Peanut oil ^d | 97.7 | 48.3 | | 19.2 | 32.5 | 66.5 | 59.1 | 17.3 | 23.1 | 0.5 |

^a Determined by the Official A.O.C.S. method (3). ^b Determination made on the fatty acids. ^c Determined spectrophotometrically (4).

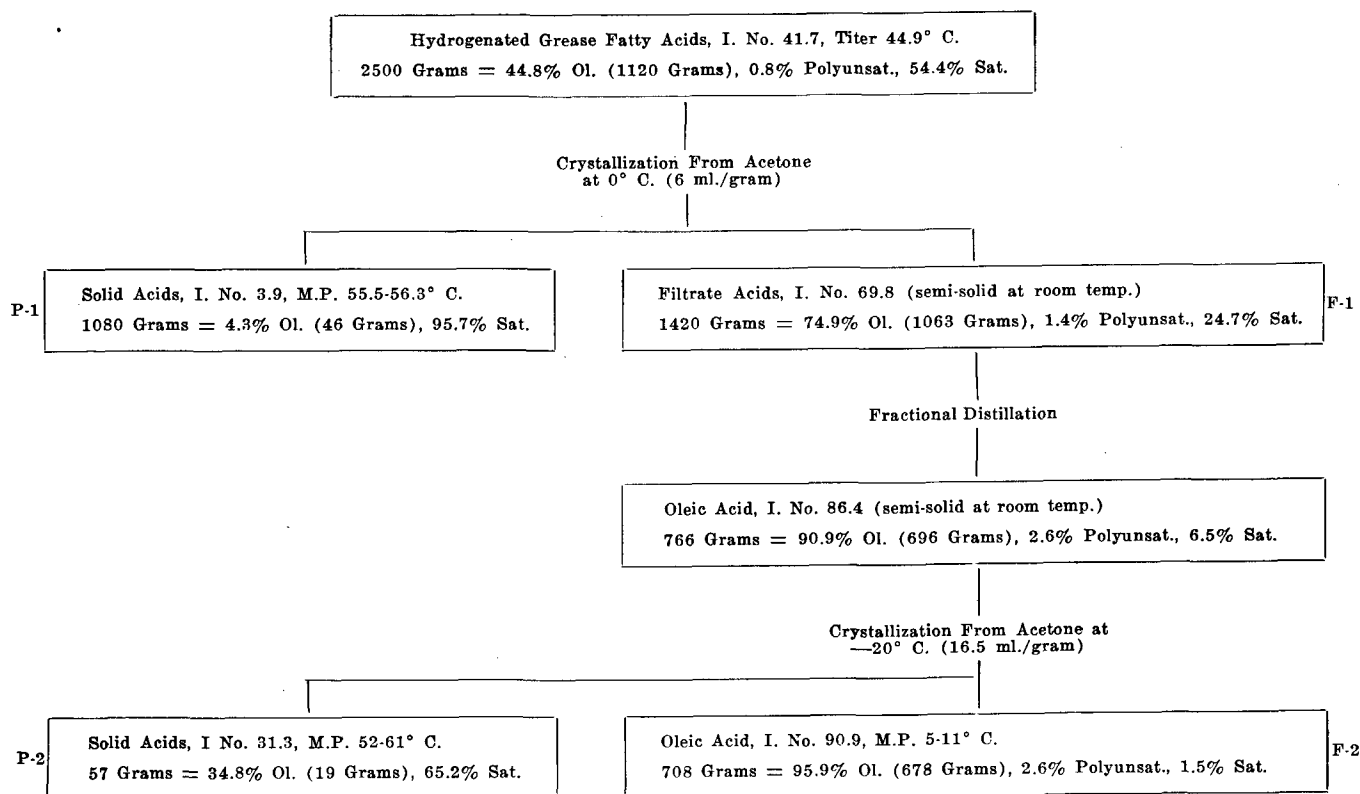
^d Data obtained from the paper by Bailey, Feuge and Smith (5).

Two purification procedures were investigated. In one the mixed fatty acids were dissolved in acetone, and the solution was cooled to 0° C. The precipitate thus obtained contained most of the stearic acid originally present in the mixed fatty acids and some of the palmitic acid but only a small proportion of the isomeric oleic acids. The acids recovered from the filtrate were semi-solid at room temperature. In order to prepare high-purity oleic acid from this product fractional distillation was required. Owing to the presence of solid isomeric oleic acids as well as saturated acids the oleic acid obtained by this distillation was also semi-solid at room temperature. Most of these impurities were separated by crystallization from acetone at -20° C. This procedure is summarized in Figure 1.

In the other procedure the acetone solution was cooled to -20° C. The precipitate contained almost all the stearic acid and most of the palmitic and

isomeric oleic acids originally present. The acids recovered from the filtrate were liquid at room temperature and were pale yellow. They contained at least 90% oleic acid. For some purposes this was sufficiently pure, but by fractional distillation a product containing at least 95% oleic acid and about 2.5% polyunsaturated acids was obtained. Starting with fatty acid mixtures containing only 0.3% polyunsaturated acids, we obtained final products containing about 97% oleic acid and about 1% polyunsaturated acids. This procedure, summarized in Figure 2, is more satisfactory than that shown in Figure 1 because the stearic acid and most of the solid isomeric oleic acids are removed in one step and the yields are better. In order to remove solid isomeric oleic acids crystallization at -20° C. is required. We have determined that above -15° C. these acids do not precipitate to any great extent from mixtures containing high percentages of oleic acid. Even when crystalli-

Preparation of Purified Oleic Acid From Fatty Acids of Selectively Hydrogenated Brown Grease
Crystallization at 0° C.



Ol. = Oleic Acids
Polyunsat. = Polyunsaturated Acids
Sat. = Saturated Acids
P, F = Precipitate and Filtrate

NOTE: The material designated as "Oleic Acids" in the solid acid fractions is mostly isomeric oleic. In all other fractions and in the starting material the oleic acid is predominantly the cis-9,10-isomer.

Fig. 1

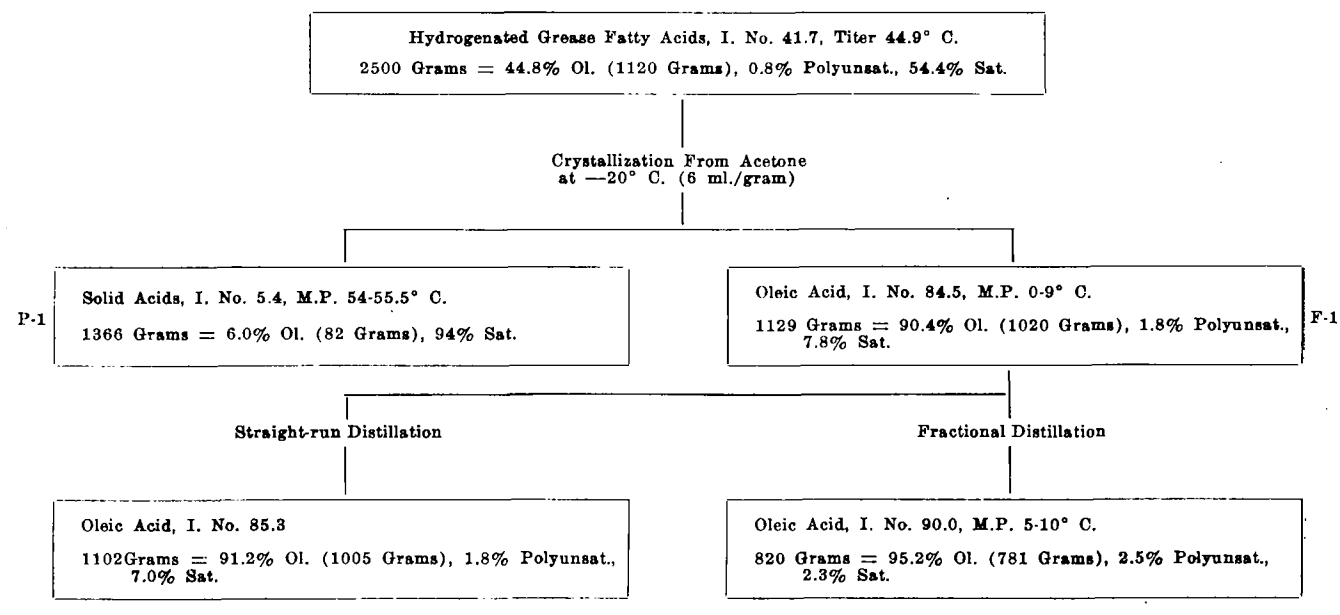
Preparation of Purified Oleic Acid From Fatty Acids of Selectively Hydrogenated Brown Grease
Crystallization at -20° C.

FIG. 2

zation at -20° C. is applied, low-melting (approximately 35° C. or less) isomers of *cis*-9,10-octadecenoic acid do not precipitate. Evidence for this conclusion was obtained by employing the technique published recently by Millican and Brown (6). Their procedure consists in converting the purified oleic acid to dihydroxystearic acid by oxidation with alkaline potassium permanganate and comparing the melting point of the dihydroxy acid obtained with that of 9,10-dihydroxystearic acid. We have found that the dihydroxystearic acid obtained from our purified oleic acid by quantitative hydroxylation with hydrogen peroxide and formic acid (7) melts about 10° C. lower than pure 9,10-dihydroxystearic acid. Since analysis of this product (neutralization equivalent and percent hydroxyl) indicates that the compound is dihydroxystearic acid, the low melting point can be explained only on the assumption that the product is a mixture of dihydroxystearic acids. Recrystallization from alcohol raises the melting point considerably, thus substantiating this assumption. We must assume therefore that the purified oleic acid contains isomeric forms although there is no doubt that *cis*-9,10-octadecenoic acid predominates.

The tallows and greases recommended as suitable starting materials for the purification processes described in this paper contain small proportions of isomeric oleic acids even before hydrogenation (6) (Table 1). In addition, selective hydrogenation increases the content of these acids, and on the basis of previously published information (8) it should probably be stopped before the polyunsaturated components have been completely eliminated if the percentage of isomeric oleic acids in the final product is to be as low as possible.

The purified oleic acid is odorless and ranges from colorless to the pale yellow, depending upon the quality of the starting material. In addition, it has remarkable color and odor stability. This suggests its use where these qualities are especially desirable, such

as in many applications in the textile industry, in cosmetics, and in pharmaceuticals. For many of these uses the presence of isomeric oleic acids would probably not be deleterious and might be decidedly advantageous. Also these purified products would be better suited for use as chemical intermediates than the oleic acid (red oil) commercially available at present.

We have found that the official method (3) of the A.O.C.S. for determining solid isomeric oleic acids is not satisfactory for determining the absolute content of these acids but is valuable only in comparing samples or in following the course of a hydrogenation by giving a rough approximation of the extent of isomeric oleic acid formation. Also, confirming the results of other investigators (9) (10), we have found that when the oleic acid content of a mixture is much above 75%, precipitation of a considerable quantity of the lead salt of *cis*-9,10-octadecenoic acid occurs. This results in an apparent isomeric oleic acid content many times higher than it actually is. For instance, when this method is applied to oleic acid prepared from olive oil, which contains little if any isomeric oleic acid, it may show a content of 20% or more. We believe that a fairly satisfactory qualitative test for the presence of solid isomeric oleic acids in purified oleic acid (oleic acid content, more than 90%) is to cool an acetone solution of the oleic acid (16.5 ml. of acetone for each gram of oleic acid in the mixture) to -20° C. and to maintain the solution at this temperature for about eight hours. The absence of a precipitate indicates that little, if any, solid isomeric oleic acid is present. If a precipitate forms, its iodine number must be determined in order to calculate the proportion of saturated acids which it contains. A solvent ratio of approximately 16.5 ml. of acetone for each gram of oleic acid in the mixture has been chosen for this test because the solubility of oleic acid in acetone at -20° C. is approximately 60 grams per liter (determined with pure oleic acid from olive oil). Of course, if the isomeric oleic acids have

low melting points, no precipitate will form; in this case, however, the lead soaps of these isomeric oleic acids will be soluble in alcohol and will not be detectable by the official A.O.C.S. method. We know of no method suitable for the quantitative determination of small quantities of such isomeric oleic acids in the presence of large quantities of oleic acid.

Experimental

Starting Material. The fatty acids used were obtained from Brown Grease which had been hydrogenated at 150° C., under a hydrogen pressure of 10 to 15 pounds per square inch and with 0.1% nickel catalyst, until its iodine number had been lowered by 10 units.³ Spectrophotometric analysis (4) revealed that the polyunsaturated acid content had been reduced to less than 1% (Table 1).

Fractionation Procedure. Crystallization at 0° C. was conducted in a refrigerated room. Crystallization at -20° C. was conducted in an electric, quick-freezing unit. Filtration of the solid acids was conducted in a table-top, Buchner funnel (O.D. about 14 inches), which was placed within a cylindrical, insulated metal container having a larger diameter than the funnel. The contents of the funnel were maintained at the desired temperatures by placing solid carbon dioxide in the annular space. Filtrations were rapid, requiring only about one to two hours for runs of the size shown in Figures 1 and 2. After removal of the acetone from the filtrate, the residue was fractionally distilled through a 5-plate Vigreux column 3 feet long and 1 inch in diameter. The results obtained are summarized in Figures 1 and 2. The boiling point of the oleic acid was about 208° C./4 mm.

Quantitative Hydroxylation of Purified Oleic Acid (7). To a well-stirred solution of 28.3 grams (0.1 mole) of oleic acid, iodine number, 90.0 (Figure 2), in 85 ml. of 98-100% formic acid at room temperature, 14.8 grams of 23.55% hydrogen peroxide (0.1025 mole, 2.5% excess) was added in one portion. The reaction became vigorously exothermic after a time lag of about seven minutes. The temperature was maintained at 40° C. with a cold water bath at the beginning and with a warm water bath toward the end of the reaction. The reaction mixture became homogeneous in about 25 minutes. After a total reaction time of two hours at 40° C. the reaction mixture was poured into a large excess of water, and the product was extracted with ether. The ether solution was washed three times with water, and the ether was evaporated. The residue was heated for one hour at 100° C. with an excess of 3 N aqueous sodium hydroxide, and the soap solution was poured into an excess of hot 3 N hydrochloric acid, with vigorous stirring. The aqueous layer was separated from the upper oily layer and discarded. The upper layer, which rapidly solidified, was melted and washed with hot water. The wash water was discarded, and the hard, white cake obtained on cooling was broken up and air-dried. The yield of crude dihydroxystearic acid was 32 grams.

³ We are indebted to the Werner G. Smith Company for supplying these fatty acids.

This was washed three times by decantation with Skellysolve B (b.p., 63-70° C.) and then filtered. The yield of dihydroxystearic acid was 29 grams (96%), m.p., 80-85° C. Neutralization equivalent: calcd., 316.5; found, 314. Hydroxyl, %: calcd. 10.8; found, 10.5. Comparable hydroxylation of pure *cis*-9,10-octadecenoic acid gave a similar yield of 9,10-dihydroxystearic acid, m.p., 92-94° C.

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Summary

A procedure is described by which a product containing at least 95% oleic acid can be prepared from animal fats. In this process crystallization of the oleic acid itself is not required, and therefore temperatures below -20° C. are not necessary. This constitutes a decided improvement over previously described processes, which require much lower temperatures.

In this procedure the fatty acids, obtained by hydrolysis of inedible tallow or grease which has been selectively hydrogenated until its content of polyunsaturates is less than 1%, are crystallized from acetone at temperatures from 0° to -20° C. to precipitate the solid acids. These acids, which amount to about 50% of the starting material, are equivalent to "double- or triple-pressed stearic acid."

The liquid acids obtained from the filtrate usually contain 90% oleic acid and when fractionally distilled yield a product containing at least 95% oleic acid. Evidence is presented to show that this purified product contains isomeric oleic acids, although *cis*-9,10-octadecenoic acid undoubtedly predominates.

The purified oleic acid is odorless and ranges from colorless to pale yellow, depending upon the quality of the starting material. In addition, it has remarkable color and odor stability. This suggests its use where these qualities are especially desirable, such as in many applications in the textile industry, in cosmetics and in pharmaceuticals. Also, these purified products would be more suited for use as chemical intermediates than the oleic acid (red oil) commercially available at present.

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