

Preparation of Pure Stearic Acid

J. M. PHILIPSON, M. J. HELDMAN, L. L. LYON, and R. D. VOLD

Department of Chemistry, The University of Southern California

IN order to interpret data on commercial soaps it is frequently necessary to investigate the behavior of systems of single pure soaps. For significant results, this often necessitates the preparation of purer fatty acids than any which can be purchased. Although there are numerous (1, 2) descriptions in the literature of methods for the preparation of pure stearic acid these all lack sufficient detail to enable even experienced workers to follow the methods without spending an excessive amount of time in trial and error development of workable procedures for the various manipulations. The procedure to be described overcomes this gap in the literature.

Previously described methods which give sufficiently pure products (99% or better) produce low yields. This makes them impractical for the preparation of the large amounts of material necessary in many investigations. This paper presents a procedure whereby 200 grams of pure stearic acid may be prepared from 500 grams of technical stearic acid.

The method used is that outlined by Hilditch in "The Chemical Constitution of Natural Fats" (3), namely the lead salt separation of the saturated from the unsaturated acids, conversion to the methyl esters, fractional distillation of the esters in vacuo, hydrolysis of the methyl stearate to stearic acid, and finally recrystallization from acetone. The authors hope that this presentation of detailed manipulative procedures will save future investigators much time and labor.

Experimental

Two 250-gram portions of technical¹ stearic acid are each dissolved in 1250 ml. of 95% alcohol contained in four liter beakers, and the solutions brought to a boil. A boiling solution of 175 grams of lead acetate (tech.) dissolved in 1250 ml. of alcohol containing 20 ml. of glacial acetic acid is added to each stearic acid solution, the mixtures boiled for five minutes and allowed to cool to room temperature. The lead stearate is filtered using suction and washed with several small portions of alcohol. Each portion of the lead salt is added to three liters of boiling alcohol, and enough glacial acetic acid is added (100-150 ml.) to bring about solution. Care must be taken at this point to prevent foaming. After cooling to room temperature, the mixtures are filtered as above, and washed with small portions of alcohol until the washings show no appreciable turbidity on dilution with distilled water. The saturated lead salts are air dried overnight and finally at 105°C. for three to four hours to remove the alcohol. At higher temperatures decomposition occurs with a resulting dark product. Each portion of the lead salts, transferred to a four liter beaker, is covered with one liter of 6N HCl, and boiled until a clear liquid layer of fatty acids floats on top. Since this may take from four to five hours,

additional hydrochloric acid should be added as needed to maintain the volume.

THE cooled solid cakes of fatty acids are broken up, combined, and dissolved in two liters of methyl alcohol containing 100 grams of sulfuric acid in a six liter round bottom flask. The solution is refluxed eight to ten hours, and the excess methyl alcohol distilled off through a Vigreux column. The remaining mixture is placed in a separatory funnel and the sulfuric acid separated from the methyl esters, which are then washed with water.

Fractional distillation² of the methyl esters is carried out under a vacuum of about 0.2 mm. in an all glass (Pyrex) column containing no stopcocks or rubber connections. The only outlet is to the vacuum line. At first the use of stopcocks was attempted but at the temperature of distillation (140-150°C.) it was very difficult to reduce the pressure to 0.2 mm., and the ordinary stopcock lubricants (apiezon, cello) contaminated the methyl stearate. The column (Fig. 1) is packed with a brass jack chain for a length of 120 cm. The procedure for distillation is as follows: the methyl stearate is poured through opening (B) into the column, the jack chain introduced, the thermometer placed in position and the opening (B) sealed off with a torch. The Fisher wax around the one liter flask is heated to 175°C. for one hour. This is

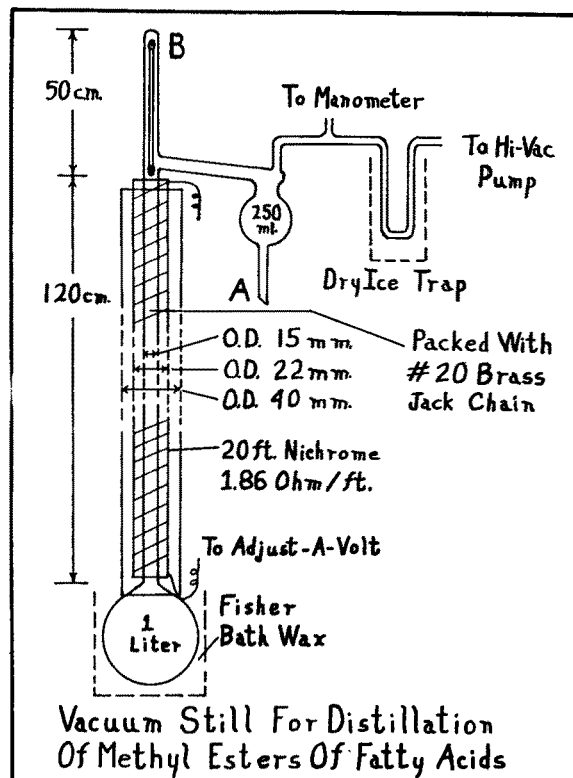


FIG. 1.

¹ It may be desirable to carry out a preliminary recrystallization from acetone. Dr. J. B. Brown suggests (personal communication) that as good or better a separation of saturated from unsaturated acids could be obtained by direct crystallization from acetone or petroleum ether as by the lead salt method. Detailed directions for such a process are given at the end of this procedure.

² See Hilditch, *The Chemical Constitution of Natural Fats*, page 373-398, for a discussion of the theory of the distillation. If much work of this kind is to be done, it would be desirable to employ more efficient but somewhat more elaborate columns as described by Longenecker, H. E., *J. Soc. Chem. Ind.* 56, 199T (1937), and by Wheeler, D. H., and Riemenschneider, R. W., *Oil and Soap* 16, 207 (1939).

done to drive out the dissolved gases in the methyl stearate. Then the vacuum is applied, current passed through the winding and the distillation begun. Distillation is carried out at the rate of 10-20 grams per hour. Refluxing must occur in the column, but care must be used to prevent flooding. This is best done by adjusting the current in the nichrome heating wire with an Adjust-a-Volt; 40-60 volts across the heating wire proved to be satisfactory. After about 50 ml. is collected in flask (A), the glass tip is broken allowing the sample to flow into a receiving flask; the tip is then sealed and the distillation continued. (All glass must be cleaned of methyl stearate before any seals are attempted, or the glass becomes too brittle to work.) Only those fractions with a freezing point higher than 36.5°C. (Beckman method) are kept for conversion to the acid. The low melting fractions are refractionated. During the first part of the distillation the brass chain was greenish as though it were oxidized on the surface, but by the middle of the distillation it became bright copper color again.

THE resulting pure methyl stearate is hydrolyzed in batches of 35-45 grams by the following procedure: The powdered or melted ester is added slowly to two liters of boiling aqueous 2.5% KOH solution in a four liter beaker; hydrolysis takes place almost immediately. The soap solution is then boiled for four hours to remove the methyl alcohol, distilled water being added as needed to maintain volume. During this time the solution must be watched carefully as there is a great tendency for bumping and foaming. The latter is conveniently controlled by additions of small amounts of cold distilled water when foaming starts. Then 6N HCl is added rapidly in large excess (about 300 ml. is convenient) and boiling is continued until the white solid acid soap originally formed is converted into a clear liquid layer of stearic acid with no specks of the solid acid soap remaining.

Each cake of cooled stearic acid is washed in distilled water, powdered, and dissolved in 500 ml. of alcohol-free ether, and the solution washed in a separatory funnel with successive portions of distilled water until the washings give no test for chloride ions. Three washings are usually sufficient. Ether is then removed from the stearic acid by warming under vacuum and the last traces of ether and water are removed by heating for an hour at 105°C.

Recrystallization from alcohol free (refluxed with KMnO₄ for 24 hours and distilled) acetone is carried out as follows: each batch of the dried stearic acid is dissolved in 500 ml. of hot acetone, filtered to remove impurities, and the filtrate chilled in ice to form small crystals. The mixture is warmed to room temperature, filtered by suction, and washed with chilled acetone. The combined filtrates may be treated further to recover more stearic acid which may be slightly less pure than the first crop.

Constants of the Stearic Acid Obtained

The effect of the foregoing purification is evident from the following comparison of constants:

	Setting point °C.	Melting point °C.	Iodine number	Equiv. weight
Original Eastman acid.....	64	64.0—66.5	3.5 ± 0.2	284.2 ± 0.5
Final purified acid.....	69.50 ± 0.02	69.7—70.0	0.0 ± 0.2	284.5 ± 0.5
Theoretical.....			0 0	284.5

The setting points were determined by the Beckman method, following deVisser's procedure (4), using a 50-100°C. thermometer graduated in 0.1°C., which was calibrated against a Bureau of Standards thermometer of the same type. In the use of the latter, directions of the Bureau of Standards were followed carefully in all respects, including the re-determination of the ice and steam points and its use at total immersion. The thermometer for setting point determinations was calibrated at the same temperature and immersion as those at which it was later used.

Capillary melting points were taken with a standard Herschberg apparatus (5). The rate of heating at the melting point was less than 1° per minute.

Equivalent weights were determined in boiling alcohol as described by Fryer and Weston (6), with a base which had been standardized against Bureau of Standards potassium acid phthalate.

Iodine numbers were determined exactly as described by Fryer and Weston (7), except that 30 ml. of CCl₄ were used to dissolve the one gram sample of acid.

IN order to estimate the purity of the acid obtained, it is necessary to compare these constants with previously reported values. Chemical constants such as iodine numbers and equivalent weights are of little value in differentiating stearic acids of relatively high purity. For example a two mole percent impurity of palmitic acid lowers the equivalent weight by only one part in one thousand, well within the experimental error. A few tenths of a mole percent impurity of oleic acid (iodine number 90.1) would give an iodine value of zero within experimental error (±0.2). None the less obtaining the theoretical value for both constants makes it highly probable that the impurities present are very largely acids. The absence of unsaturates was further shown by the lack of color upon solution in concentrated sulphuric acid.

The capillary melting point was determined for comparison with previous literature values, which vary widely as would be expected. The limitations of this constant make it useful only for comparative purposes.

The highest reported setting point for stearic acid is 69.60°C.(1). This is assumed to be 100% stearic acid for the following discussion. From the heat of fusion, about 13,500 calories per mole (8), the calculated lowering of the setting point is about 0.2°C. per mole percent impurity. Francis, Collins, and Piper (9) found a lowering of 0.24°C. per mole percent of palmitic acid, in fair agreement with the calculated value. Assuming, as is reasonable from the above, that the impurities in the present acid are homologous and do not form solid solutions, the latter is at least 99.5 mole percent pure.

The above arguments show, in agreement with Francis and Piper (2), that the setting point is the most useful constant for comparison of the purity of various stearic acids. On this basis, the only purer acid ever reported was the two grams, a 4% yield, obtained by Guy and Smith (1). The preparation of Francis and Piper (10) had a setting point of only 69.39°C. Both of these preparations involved many recrystallizations, 24 for the former. The present

method avoids this drudgery, and makes it feasible to prepare large amounts of the pure acid in good yields from poor starting materials.

REFERENCES

- (1) J. B. Guy and J. C. Smith, *J. Chem. Soc.*, 1939, 615.
- (2) F. Francis and S. H. Piper, *J. Chem. Soc.*, 1936, 137.
- (3) T. P. Hilditch, *The Chemical Constitution of Natural Fats*, John Wiley and Sons, New York, (1941).

- (4) L. E. O. de Visser, *Rec. trav. Chim.*, 17, 182, (1898).
- (5) E. B. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, 8, 312, (1936).
- (6) P. J. Fryer and F. E. Weston, *Oils, Fats, and Waxes*, Camb. Tech. Series, (1939).
- (7) P. J. Fryer and F. E. Weston, *Oils, Fats, and Waxes*, Camb. Tech. Series, P. 92, (1939).
- (8) *Int. Crit. Tables*, 5, 137, (1929).
- (9) F. Francis, P. J. E. Collins and S. H. Piper, *Proc. Roy. Soc. (London)*, A 158, 691, (1937).
- (10) F. Francis and S. H. Piper, *J. Am. Chem. Soc.*, 61, 577, (1939).

Gamma-Tocopherol as a Precursor of a Red Quinoid Substance Developed in Cottonseed Oil During Oxidation¹

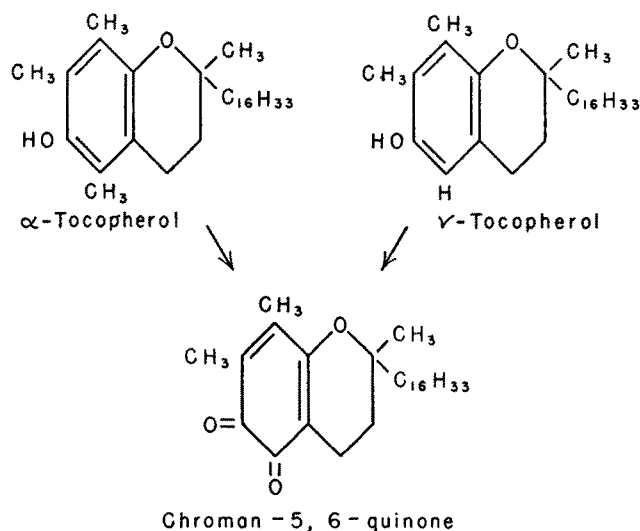
C. E. SWIFT,² G. E. MANN, and G. S. FISHER

Southern Regional Research Laboratory³
New Orleans, Louisiana

Introduction

THE development of a red color in cottonseed oil during oxidation was observed by Wheeler (10) and Freyer (3). Golumbic (5,6) reported the recovery, from fresh and incipiently rancid cottonseed oil, of a red, oily, antioxygenic substance, exhibiting the behavior of chroman-5,6-quinones. He concluded that the quinoid substances observed in oxidized fats were products of oxidation of colorless precursors. He stated that "the colorless precursors of these quinoid compounds are not the tocopherols" since "the quinoid compounds were never detected in autoxidizing animal fats or in purified fat substrates containing only added tocopherol." This and supplementary evidence were interpreted as indicating the occurrence of a newly discovered "tocol" constituent in cottonseed oil.

Smith (9) has shown that red chroman-5,6-quinones are formed when 6-hydroxychromans are oxidized with nitric acid. On the basis of the similarity of absorption spectra (1,8), α - and γ -tocopherols presumably form identical chroman-5,6-quinones when oxidized by nitric acid, as indicated in the following formulas:



If the hydrogen occupying the 5-position in γ -tocopherol is more readily removed by oxidation than the methyl group occupying the same position in α -tocopherol, it might be assumed that under milder conditions of oxidation, such as oxidation with air in the presence of a fat, γ -tocopherol but not α -tocopherol, might be oxidized to form a chroman-5,6-quinone. This possibility has apparently not been investigated, or at least has not been reported by Golumbic (5,6). Consequently, an investigation was undertaken to determine the possible role which γ -tocopherol plays in the development of red quinoid color of oxidizing fats. It had been previously observed in connection with other investigations of the mechanism of fat oxidation that cottonseed oil and other fats, when subjected to accelerated oxidation, developed a red color having an absorption maximum at 470 $m\mu$. It was further observed that when γ -tocopherol was added to a fat relatively free of natural antioxidants and aerated at elevated temperature, a similar red color was developed which was also found to have an absorption maximum at 470 $m\mu$. The following experimental work amply substantiates the assumption that γ -tocopherol is actually a precursor in the development of the red color of oxidizing fats in which this substance is present.

Preparation of Reactants and Methods Used

(a) *Synthesis of chroman-5,6-quinone*: Chroman-5,6-quinone [2,7,8-trimethyl-2-(4',8',12'-trimethyl-tridecyl-1)-chroman-5,6-quinone] was synthesized as follows: To synthetic *d,l*- α -tocopherol [1 gm., Merck, $E_{1\text{cm}}^{1\%}$ (292 $m\mu$) = 70] in absolute ethanol (900 ml.), concentrated nitric acid (100 ml.) was added. The mixture was heated at 70° C. until measurements of the spectral absorption at 470 $m\mu$ indicated that the concentration of the red product had reached a maximum, which occurred in about 50 minutes. The alcoholic solution of the reaction mixture was poured into 2.5 liters of ice water and the reaction product

¹ Presented before the American Oil Chemists' Society Meeting, New Orleans, Louisiana, May 10 to 12, 1944.

² National Cottonseed Products Association Fellow.

³ This is one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.