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The Preparation of Stearic Acid from Castor Oil[1]

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SOURCE materials for the preparation of stearic acid are (a) lards and tallows and certain tropical vegetable oils of which it is a prominent component, such as cocoa butter, Borneo tallow, and shea nut butter, and (b) oils rich in C_{18} unsaturated acids. The point of departure for some investigators whose objective had been the preparation of the pure acid is the technical product which presumably would have been prepared from any of these. Guy and Smith (2), for example, sacrificing quantity for quality—the yield was only 4% — by following a laborious procedure involving 24 crystallizations and three distillations succeeded in preparing pure stearic from the "purest" commercial acid. Philipson *et al.* (3) have presented detailed manipulative procedures, based on the well known lead salt-alcohol separation of the unsaturated from the saturated acids, for preparing from technical stearic acid the pure product in 40% yield. Our own experiences in the preparation of a stearic acid meeting the requirements of a primary standard for research purposes have emphasized the desirability of making the point of departure of such a preparation a vegetable oil which is not only practically devoid of C_{16} and other saturated acids but is also readily altered by procedures with which those skilled in the techniques of organic syntheses are familiar. Castor oil, a substantial amount of whose fatty acids is ricinoleic, or 12-hydroxy-Δ-9:10-octadecenoic acid, meets these requirements.

By taking advantage of the fact that the glycerides of castor oil are readily saturated by catalytic hydrogenation over Raney nickel and utilizing the relative

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insolubility of the ethyl ester of 12-hydroxystearic acid in hydrocarbon solvents, one may obtain the pure material from which by de-hydroxylation via its halogeno derivative and recrystallization of the product from acetone there results exceptionally pure stearic acid. Yields of at least 40%, based on the weight of the castor oil used, are possible.

How the several steps outlined above were accomplished is described in the following paragraphs.

Experimental Procedure

12-Hydroxystearic Acid. A filtered, one-liter ethanol solution of castor oil (58 g.) completely saturated by catalytic hydrogenation over Raney nickel at 150° for 30 minutes was heated under a reflux for eight hours with sulfuric acid (20 g.). The solution was cooled and the ester removed by filtration. More ester was obtained from the filtrate upon the addition of 100 cc. of water. The combined ester crops were recrystallized from 300 cc. of petroleum ether (b.p. 60-69°) whereupon 45.8 g. of ethyl-12-hydroxystearate were obtained.

The hydroxy ester was saponified and the liberated acid recrystallized, first from benzene and then from petroleum ether. A marked tendency to form gels in solution made further purification desirable. The brownish solid (39 g.), comminuted in a mortar, was then washed with cold petroleum ether, a loss of only 0.1 g. per 12-gram portion resulting. A considerable improvement in color was noted. The 12-hydroxystearic acid thus purified had a melting point of 80.5-80.9°.

12-Iodostearic Acid. 12-hydroxystearic acid (11.9 g.), red phosphorus (.45 g.) and iodine (5.9 g.) were heated at 100 to 125° for three hours with vigorous stirring. The mixture was transferred to a separatory funnel with 300 cc. of warm petroleum ether, washed with water and 5% sodium sulfite solution, dried with calcium chloride and filtered. The solvent was removed by distillation.

Stearic Acid. The 12-iodostearic acid was not isolated but was converted to stearic acid by refluxing it with 250 cc. of glacial acetic acid with the addition of one-gram portions of zinc dust at half-hour intervals until four grams had been added. Unreacted zinc was filtered off after which the filtrate was diluted to four times its volume with water. After the solution had been cooled to room temperature, the precipitated white stearic acid (10.8 g. after being dried) was dissolved in 300 cc. of acetone, treated with charcoal, filtered, and crystallized. Eight grams of stearic acid having a solidification point (2) of 69.06° were obtained. Recrystallization of the product from 200 cc. of acetone resulted in a yield of 7.3 grams with a solidification point of 69.33°. Based on the weight of castor oil used, this represents a yield of approximately 40 per cent.

Summary

By de-hydroxylating the 12-hydroxystearic acid, which may be prepared in a pure state by the alcoholysis of fully hydrogenated castor oil, there may be obtained in at least 40% yield an exceptionally pure stearic acid whose solidification point is the same as that of a similar product previously reported by others (1). Avoided by the procedure described are recourse to the necessity of preparing lead soaps for the removal of unsaturated fatty acids and the drudgery of repeated crystallizations as prescribed by other published methods.

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Dilatometric Investigations of Fats

IV. Estimation of Solids and Liquid in Some Plastic Fats

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A PREVIOUS publication (3) from this laboratory has reported the results of a calorimetric estimation of solids and liquid in a plastic sample of hydrogenated cottonseed oil. As pointed out by Hofgaard (6), estimates of solids and liquid may be made equally well from dilatometric data since considerable changes in volume accompany melting or solidification of a fat. During the present investigation dilatometric estimates of the proportions of solids and liquid at different temperatures were made upon the sample of hydrogenated cottonseed oil previously examined in the calorimeter and also upon three additional plastic fats. These are believed to be the first reasonably reliable data of their kind. The previous data of Hofgaard (6) are rendered inaccurate by failure to work at temperatures low enough to attain complete solidification of the samples and by an assumption regarding the applicability of Tammann's rule to fatty materials which has been shown to be unjustified (4).

The Fat Samples

Each of the fats examined was a heterogeneous material which contained both solids and liquid over a wide range of temperature. The cottonseed oil was partially hydrogenated and was from the batch previously analyzed calorimetrically for solids and liquids at different temperatures. At ordinary room temperature it was slightly firmer in consistency than most commercial shortenings or margarine oils. The prime steam lard was a commercial sample, with no hardened

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