anisole, alone or in combination with propyl gallate and citric acid, is an effective antioxidant for cooking potato chips in vegetable oils, vegetable shortening, and combinations of these with lard. Particular attention should be called to the combination of 60% vegetable shortening and 40% lard. This produced a chip of stability approximately equal to that cooked in vegetable shortening and of far superior stability to chips fried in cottonseed oil alone or in a vegetable shortening-cottonseed oil blend. The ratio of 60% vegetable shortening to 40% lard was decided upon after several laboratory experiments with varying percentages of lard in the frying fat. Forty per cent lard seems to be an optimum for best processing characteristics and flavor of final product. Of equal interest is the fact that the life of potato chips fried in pure cottonseed oil can be doubled by the use of butylated hydroxyanisole as antioxidant. It also should be pointed out that, in the one set of experiments where direct comparison is possible, the use of the combination antioxidant provided slightly greater stability in potato chips than the use of butylated hydroxyanisole alone.

Summary

Laboratory and commercial-scale fryings of potato chips have been made with various vegetable oils, vegetable shortenings, lard, and combinations of these. Fryings have been made with and without the addition of butylated hydroxyanisole as an antioxidant. The data from both types of experiments indicates that butylated hydroxyanisole possesses "carry-through" antioxidant properties not only in animal fats but in vegetable oils and vegetable shortenings also. Data also indicates that the addition of propyl gallate and citric acid as synergists to the butylated hydroxyanisole increases the "carry-through" antioxidant properties.

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The Synthesis of 12-Ketostearic Acid

OLIVER GRUMMITT and K. G. SIEDSCHLAG,* Western Reserve University, Cleveland 6, Ohio

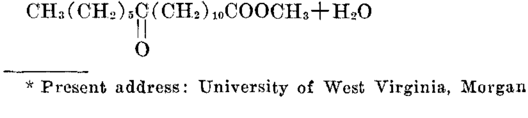
A MAJOR trend in fat and oil technology is the commercial development of valuable chemical derivatives. In addition to acids of increasing degrees of purity, such acid derivatives as amines, amides, and nitriles are now available. A variety of non-ionic surface active agents are being made directly or indirectly from fatty acids. Castor oil is a well known raw material for the synthesis of n-heptaldehyde, octanol-2, and sebacic acid.

Our need for a saturated long-chain keto acid with the ketone group close to the center of the chain stimulated a study of the possibility of making 12-ketostearic acid from castor oil. While such a synthesis is not new (1), the literature showed that detailed directions for a laboratory scale preparation were not available. Since this acid may be of interest to others and since this preparation may point the way to larger scale production, the method is given here.

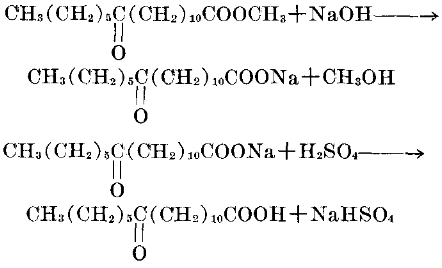
This preparation involves the methanolysis of castor oil to methyl ricinoleate, catalytic reduction to methyl-12-hydroxystearate, oxidation by chromic acid to methyl-12-ketostearate, and saponification and acidification to give 12-ketostearic acid:

$$\text{Castor oil} + CH_3OH \xrightarrow{H_2SO_4} CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOCH_3 + C_3H_5(OH)_3$$

$$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOCH_3 + H_2 \longrightarrow CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOCH_3$$



$$CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOCH_3 + (O) \xrightarrow[AcOH]{CrO_3} CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}COOCH_3 + H_2O$$



$$CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}COOCH_3 + NaOH \longrightarrow CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}COONa + CH_3OH$$

$$CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}COONa + H_2SO_4 \longrightarrow CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}COOH + NaHSO_4$$

Experimental

Dissolve 4 g. of concentrated sulfuric acid in 300 ml. (237 g., 7.4 moles) of methanol (99-100% pure). To this solution add 200 g. (0.21 mole) of a refined grade of castor oil. (The average molecular weight of castor oil was considered to be 940.) This mixture is refluxed on the steam bath for four hours with occasional shaking, cooled, and poured into one liter of water with stirring. The oil layer is washed with 100-ml. portions of water until the wash water is neutral to litmus. This washing step is important because residual traces of sulfuric acid will catalyze dehydration of the methyl ricinoleate during distillation.†

The crude methyl ricinoleate is distilled at 3- to 4-mm. pressure, discarding the first 25 ml. and collecting as product the 170-195° fraction. The distillate weighs 150-160 g., which is an 87-93% yield based on the assumption of an 87% concentration of ricinoleic acid in the castor oil (1a).

Analysis of the methyl ricinoleate by saponification number (A.O.C.S. Official Method Cd 3-25),

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* Present address: University of West Virginia, Morgantown, W. Va.

† One authority has pointed out that an alkali-catalyzed methanolysis would have the advantage of simplifying this washing step and reducing the danger of dehydration.

iodine number (Wijs, 60-minute), and hydroxyl content (1b) indicated a purity of 90-94%. Analysis of a typical product gave a saponification number of 181.5 (calculated, 179.5), iodine number 81.9 (calculated 81.0), and hydroxyl content 5.15% (calculated 5.44%).

Add to 150 g. (0.48 mole) of the methyl ricinoleate 0.5 g. of Adam's platinum black catalyst (2) and hydrogenate in a Parr low-pressure hydrogenator (3) until no more hydrogen is absorbed. This will require a pressure drop of about 40 pounds and a reaction time of 3-4 hours. An infrared bulb placed about 12 inches from the bottle will keep the reaction mixture molten during the hydrogenation. The molten reduced product is filtered with suction through a steam-jacketed Büchner funnel to remove all or most of the catalyst. If further clarification is necessary, 0.5 ml. of 10% sodium hydroxide is added to the filtrate, and the mixture is heated and stirred on the steam bath for 15 minutes. Then 2 g. of Norit are added, the heating and stirring are continued for 15 minutes more, and the mixture is again filtered with suction. On cooling, the methyl-12-hydroxystearate crystallizes to give 142-146 g., 94-97%, melting 53-54°. This product need not be purified to make 12-ketostearic acid.

A single crystallization from methanol will give 72 g. of acid, melting 56-57°. This was done by dissolving the acid in 100 ml. of refluxing methanol, adding 1-2 g. of Norit, refluxing for a few minutes, filtering the hot solution, and cooling to 0°. Bickford *et al.* report 57.0-57.5° as the melting point of the pure ester (4).

The methyl-12-hydroxystearate is oxidized as follows: In a one-liter, three-necked flask fitted with a stirrer, reflux condenser, 500-ml. dropping funnel, and a thermometer suspended through the condenser into the flask are placed 142 g. (0.45 mole) of ester and 130 ml. of glacial acetic acid. A solution of 45 g. (0.45 mole) of technical chromic acid in 350 ml. of hot glacial acetic acid is added from the funnel to the stirred ester solution at such a rate that the temperature does not exceed 70°. This addition requires 30-40 minutes. Heating at 70° and stirring are continued for three hours. After cooling, the mixture is poured with stirring into two liters of cold water, and the crude methyl-12-ketostearate is collected by suction filtration. The solid is washed with three 200-ml. portions of water, 200 ml. of 5 % sodium carbonate solution, and then with three 200-ml. portions of water. After drying in air, the crude product weighs 121-127 g., 86-90%, m.p. 43-45°. This product need not be purified to make 12-ketostearic acid. A single crystallization from 250 ml. of methanol with 1-2 g. of Norit, as described for the methyl-12-hydroxystearate, will give 50 g., melting 45-46°. Reduction of the volume of the mother liquor by one-half gives 28 g., melting 43.5-45.5°.

The methyl-12-ketostearate, 121 g. (0.39 mole), is saponified by heating at reflux for two hours with 32 g. (0.57 mole) of potassium hydroxide dissolved in 350 ml. of 95% ethanol. The mixture is cooled and neutralized to litmus with 150-170 ml. of 20% sulfuric acid, followed by the addition of 40 ml. of this acid. The crude 12-ketostearic acid is suction filtered and washed with 200-ml. portions of water until the filtrate is free of acid. After air drying, the product weighs 107-111 g., 93-96%, m.p. 77-80°. Crystallization from 330 ml. of methanol plus 23-25 ml. of water at the boiling point and treatment with 1-2 g. of Norit, as described before, gives 95-99 g., 82-86%, m.p. 80-81°.

The over-all yield based on castor oil is 65% if the minimum yield is obtained in each of the four steps, and 78% if the maximum yield is obtained.

Discussion

Other synthetic routes to 12-ketostearic acid described in the literature include the thermal decomposition of barium ricinoleate (5), catalytic isomerization of castor oil in the presence of palladium, nickel, or copper followed by saponification, etc. (6), and the reaction of n-hexylmagnesium bromide with 11-bromo-1-undecanonitrile, conversion of the bromide to the nitrile, and hydrolysis of the nitrile (7).

Summary

A synthesis of 12-ketostearic acid in 78% yield from castor oil by methanolysis to methyl ricinoleate, reduction to methyl-12-hydroxystearate, oxidation to methyl-12-ketostearate, followed by saponification has been described in detail.

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