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Note on the Synthesis of Symmetrical Triglycerides[1,2,3]

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IN a project in this laboratory it became necessary to prepare relatively large quantities of symmetrical oleodistearin, oleodipalmitin, stearodiolein, palmitodistearin, and stearodipalmitin. Since their preparation is costly and time-consuming, considerable attention was given to improving previously described methods (1, 2, 4, 5, 8, 9, 11, 13, 14, 15, 16, 17) so that better yields might be obtained. Using procedures described in the following paragraphs to prepare the desired compounds from monotrityl glycerol and the fatty acid chlorides, overall yields between 70 and 80% were obtained based on the original pure fatty acids, which in some cases doubled yields obtained by the best of the previously reported methods.

The alpha monotrityl glycerol used in these syntheses was prepared as outlined by Verdake and Meerburg (15). In this step trityl chloride (triphenylmethyl chloride) prepared in the laboratory (12) was a more satisfactory starting material than any of the commercial samples that were tried.

Preparation of fatty acid chlorides. Highly purified samples of fatty acids prepared by conventional methods were used. On the basis of investigations by Bauer (3) phosphorous pentachloride was used as a chlorinating agent for palmitic and stearic acids, and oxallyl chloride or phosphorous trichloride were used as chlorinating agents for oleic acid. The improved yields of acid chlorides were found to be due primarily to improved distillation techniques.

The procedure which was employed for the preparation of stearoyl chloride is typical of those used with all of the fatty acids and chlorinating agents. One hundred grams (0.35 mols) of stearic acid were placed in a 1-liter, 3-necked flask equipped with a condenser and stirrer and partially immersed in a water bath at 70°C. One hundred ten grams (0.51 mols) of phosphorous pentachloride were added over a period of one-half hour. The mixture was stirred for 2½ hours and then poured into a 500-ml. Claisen flask. The Claisen flask was placed in an oil bath and the distillation forerun was removed under the vacuum of a water aspirator while the bath temperature was raised to 140°C. The residual liquid was carefully decanted from the yellow solid into a clean flask, and the latter was connected to a water-cooled receiver and a mechanical vacuum pump system. The temperature of the oil bath was raised to 235°C., i.e., approximately 40° above the boiling point of the stearoyl chloride at 4 mm. of mercury pressure and the flask then immersed up to the distilling arm. The distillation was carried out as rapidly as possible. This procedure very substantially reduced the loss of fatty acid chloride that ordinarily occurs during distillation. The product was colorless and almost odorless.

The yields of fatty acid chlorides are reported in Table I and show improvements over yields previously reported for smaller quantities of fatty acids, particularly in the chlorination of oleic acid by phosphorous trichloride.

The free fatty acid contents of the stearoyl and oleoyl chlorides were determined by the procedure given by Bauer (3) and were found to be 2.2 and 1.4%, respectively.

TABLE I

Yields of Fatty Acid Chlorides and Distillation Temperatures

Fatty acid	Chlorinating reagent	Yield from 100 g. fatty acid	Yield obtained by Bauer (30) from 20 g. fatty acid	Distillation temperature
		%	%	
Stearic acid	PCl_5	97.8	77.2	192° at 4 mm. Bath temp. 225°
Palmitic acid	PCl_5	98.5	88.9	180° at 4 mm. Bath temp. 220°
Oleic acid	$(COCl)_2$	94.7	76.3	193° at 4 mm. Bath temp. 230°
Oleic acid	PCl_3	89.2	56.8	188° at 3 mm. Bath temp. 230°

Synthesis of symmetrical diglycerides. The procedure described by Daubert and co-workers for the synthesis of symmetrical distearin (8) and diolein (5) was used in modified form to prepare the saturated symmetrical diglycerides. A 5% excess of fatty acid chloride was sufficient to produce a good yield. One hundred and ten grams of stearoyl chloride were added slowly to 57 grams of monotrityl glycerol dissolved in 330 ml. of dry chloroform and 80 grams of dry pyridine. The reactants were allowed to stand at room temperature for an hour and were then refluxed for 12 hours. The mixture was cooled to room temperature, dissolved in diethyl ether, and washed successively with water, 0.5 N sulphuric acid cooled to 0°C., 5% aqueous sodium carbonate, and water. The ether solution was dried over anhydrous sodium sulfate and the ether removed under vacuum. The resulting oil was dissolved in petroleum ether(Skellysolve F) and cooled in an ice bath to 0°C. Dry hy-

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[2] Submitted as part of Ph.D. thesis by B. M. Craig, University of Minnesota, 1950.

[3] Presented at meeting of the American Oil Chemists' Society, San Francisco, September, 1950.

drogen chloride was passed into the solution for 0.5 hour. The solution was allowed to stand at room temperature for one hour. Sufficient ethyl ether was added to dissolve the products, and the ether solution was washed with 5% aqueous sodium carbonate and water. The symmetrical distearin was crystallized from the ether solution and was then purified by several recrystallizations from acetone.

The use of ethyl alcohol as a solvent for the recrystallizations was avoided because it was found that the ethyl ether of triphenyl carbinol (melting point 82°C.), produced through the reaction of the trityl compounds with ethyl alcohol, interfered with the separation of the pure diglycerides.

The same procedure was followed for the preparation of symmetrical diolein except that the trityl compounds formed by the acid hydrolysis were separated from the diolein by crystallization from petroleum ether (Skellysolve F) solution. The solution was then washed with 5% aqueous sodium carbonate and water and the petroleum ether removed under vacuum. The crude diolein was dissolved in acetone, refluxed with decolorizing carbon for 10 minutes, filtered, and purified by several crystallizations from acetone.

The yields of symmetrical distearin and diolein were 87 and 90% respectively and were considerably higher than the yields that were obtained in this laboratory by the methods previously referred to (5, 8).

Preparation of symmetrical mixed triglycerides. The procedure outlined by Daubert and co-workers (8) for the synthesis of symmetrical triglycerides was employed with a modification similar to that described for preparation of the symmetrical diglycerides. The modified procedure will be exemplified by describing the preparation of symmetrical oleodistearin.

Eighty-five grams of distearin were dissolved in 125 g. of pyridine and 365 ml. of chloroform. Forty-three grams of oleoyl chloride (5% excess over the stoichiometric proportion) were added slowly and the mixture was allowed to stand at room temperature for one hour, then refluxed for 12 hours, cooled to room temperature, and dissolved in ethyl ether. The ether solution was washed with water, 0.5 N sulphuric acid solution at 0°C., 5% potassium carbonate solution, water, and then dried over anhydrous sodium sulphate. The ether was removed under vacuum and the crude oleodistearin dissolved in acetone. Decolorizing charcoal was added, the solution was refluxed for 15 minutes, and then filtered. The oleodistearin was recrystallized from the clear solution and purified by further crystallizations from acetone. The yield of pure symmetrical oleodistearin was 107 g. (91% of the theoretical). Similar yields were obtained in the preparation of the other mixed triglycerides.

Table II compares some observed iodine values and melting points of the diglycerides and symmetrical mixed triglycerides with theoretical values or with values previously reported by others for the pure compounds.

TABLE II

Properties of Diglycerides and Triglycerides

Glyceride	Wijs iodine value		Melting point °C. capillary tube	
	Observed	Theoretical	Observed	Reported
1,3 distearin	0	0	79.0	79.6(8)
1,3 dipalmitin	0	0	72.0	72.5(8)
1,3 diolein	81.7	81.8	......	......
Oleodistearin	28.7	28.6	38.5, 42.5[a]	38.5, 42.5(8)
Oleodipalmitin	30.5	30.7	35.5	35.5-36.5(8)
Stearodiolein	57.1	57.2	23.5	......
Palmitodistearin	0	0	67.7	68.0(10)
Stearodipalmitin	0	0	67.7	68.0(10)

[a] Oleodistearin melting at 38.5°C. when held in capillary tube at 40° C. for 48 hours, solidified and gave a m.p. 42.5°C.

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Protein Denaturation in Soybean Meal During Processing

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THE steady increase in industrial utilization of soybean proteinaceous materials during the last decade has focused attention on the effect of oil solvent extraction on the properties of the meal. Denaturation of the proteins in soybean meal is inherent in soybean processing because of the necessity of applying heat in the presence of moisture. The extent of denaturation determines the physical, chemical, and nutritional properties of the meal. These imposed characteristics govern to a large extent the ultimate industrial application of the processed meal. The manufacture of soybean meals with different degrees of heat treatment and the judicious application of such meals can result in increased revenue for the processor.

Protein denaturation has been defined by Neurath, Greenstein, Putnam, and Erickson (8) as "any non-

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