High-Yield Preparation of Methyl Stearolate [1]

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Abstract

A simplified laboratory procedure for preparing methyl stearolate consists of three steps—bromination, dehydrobromination, and purification. A variety of starting materials was investigated, including oleic acid, olive fatty acids, and triglycerides. Brominations of both fatty acids and triglycerides were conducted in diethyl ether. Dehydrobrominations were carried out in boiling 30% KOH–ethylene glycol solutions or in 30% KOH–water solutions under pressure. Saponification of the triglycerides also occurred at this step. After conversion to methyl esters and distillation, the product from olive oil analyzed 79% methyl stearolate. Purification was accomplished by either argentation or acetonitrile-hexane countercurrent distribution and yielded methyl stearolate of +99% purity. Over-all recoveries, based upon the amount of oleic acid present in the initial oil, averaged 80%. In addition to the laboratory procedure, possible production operations are outlined.

Introduction

A METHOD OF PREPARING methyl stearolate (methyl 9-octadecynoate) has been described by Ames and Covell (2) in which the main reaction is the condensation of 9-bromononanoic acid with an excess of 1-lithio-1-nonyne in liquid ammonia-tetrahydrofuran. Since preparation of the starting materials is difficult, their procedure is not routinely used. More generally, stearolic acid is prepared by bromination, dehydrobromination, and crystallization of oleic acid. Adkins and Burks (1) obtained a 33–42% yield by a procedure in which they brominated oleic acid directly, dehydrobrominated with a KOH–*n*-amyl alcohol solution, and crystallized from an ethanol-water system. Khan (7–9), who reported difficulty in reproducing the work of Adkins and Burks, brominated oleic acid in a diethyl ether solution, dehydrobrominated with sodamide in liquid ammonia, and crystallized from petroleum ether (PE) several times, achieving a yield of 68–78%. Also, Khan (8) reported using olive oil, corn oil, and soybean oil acids as starting materials. The only change in his procedure was the incorporation of urea crystallizations which were repeated five times before the final PE crystallizations. The added crystallizations reduced over-all yield to 44–58% of theoretical.

The laboratory procedures incorporating pure oleic acid, sodamide in liquid ammonia, or many crystallizations are not easily scaled up. Because of a need for large amounts of methyl stearolate for hydrogenation studies, a shorter, simpler, higher yielding preparation procedure embodying relatively crude sources has been devised.

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Experimental

Bromination

Oleic acid, olive fatty acids, and olive oil were brominated by slowly adding a slight excess of liquid bromine to a well-stirred 20% ether solution while maintaining the temperature below 20C. The ether and excess bromine were removed under vacuum. In addition, olive triglycerides were also brominated without solvent and the excess bromine was not removed before dehydrobromination.

Dehydrobromination

A fourfold excess of 30% aqueous KOH was added to the brominated oil. The reaction was heated in a Paar pressure reaction vessel to 180C with constant stirring. After 4 hr at this temperature, the vessel was cooled. The resulting soap cake was skimmed off the liquor, dissolved in warm water, and filtered to remove the carbon formed during the reaction. The filtrate was then acidified with concentrated HCl, and the precipitate formed was removed by filtration, dissolved in PE, and dried; after PE was removed by vacuum, crude stearolic acid remained.

Ethylene glycol dehydrobrominations were carried out by refluxing a fourfold excess of a 30% solution of KOH in this solvent with the brominated oils for 6 hr. The solution was then cooled, acidified with dilute HCl, extracted with PE, washed, and dried; PE was removed under vacuum to yield crude stearolic acid.

Esterification

Fatty acids were esterified by the acid-catalyzed esterification procedure of Luddy et al. (10). The methyl esters of the crude stearolic acid were distilled at 0.05 mm Hg to remove any polymers or unesterified acids.

Gas Chromatographs

Chromatographs were run on a 1/8 in. by 5 ft stainless steel column packed with 25% stabilized DEGS on 60/80 Chromosorb. A flame ionization detector was used. Samples taken during dehydrobromination were esterified before being chromatographed. Dehydrobromination samples were temperature programmed from 150–225C at 4°/min and held at 225C until the dibromocompound eluted. Countercurrent distribution samples were run isothermally at 180C.

Countercurrent Distribution

A 200-tube automatic countercurrent distribution (CCD) apparatus in which each tube contained 40 ml of lower layer solvent and 10 ml of upper layer solvent was used. The distributions were made according to the single withdrawal procedure (12). Solvent systems were acetonitrile-hexane (12) and 0.2 N $AgNO_3$ in 90% methanol-hexane (11). A recording refractometer was used to monitor the effluent upper solvent layer (4,5).

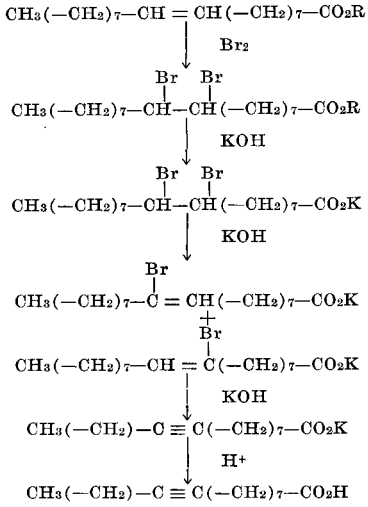
Crystallization

All crystallizations of methyl esters were done in an ethanol-water system. To a room temperature

solution of 10% sample in 95% ethanol, water was added slowly until the solution remained cloudy. It was warmed until the solution cleared and then crystallized at 0C. The stearolate resulting is concentrated in the crystals.

Results and Discussion

The reactions involved in the preparation of stearolic acid are:



The first step, bromination of unsaturated fatty acids, is done in a nonreactive solvent, such as diethyl ether, so that the reaction medium is homogeneous. Fatty esters and triglycerides, which are liquid at reaction temperatures, can be brominated without solvent; however, strong mechanical stirring is required since viscosity increases with bromination. In the laboratory, it is preferable to use a solvent to reduce the viscosity.

The bromination reaction is essentially quantitative when carried out in glassware; when conducted in stainless steel vessels, however, bromination is incomplete even when a 10% excess of bromine has been added. Since the stainless steel vessels we used were high in chromium content, this incomplete reaction could possibly be owing to an oxidative coupling reaction between the chromium and bromine. When a solvent is used, the effect of the stainless steel is reduced and the reaction is more complete.

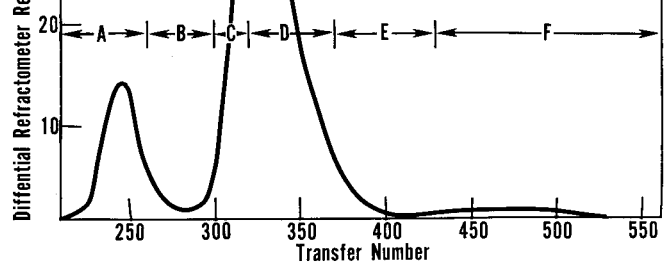


FIG. 1. Countercurrent distribution of crude methyl stearolate from olive oil with 10 ml of *n*-hexane and 40 ml of 0.2 N $AgNO_3$ in 90% aqueous methanol as the solvent system.

TABLE I
Time Course of Aqueous Dehydrobromination

Time, min	Temp, C	Composition (%)		
		Dibromo	Monobromo	Stearolic
0	27	100.0	.....	.....
25	120	93.6	6.4	.....
32	145	82.9	17.1	.....
42	162	58.5	50.8	3.1
52	160	29.0	65.4	5.6
72	156	2.1	86.0	11.9
112	166	.....	60.2	39.8

Dehydrobromination of esters is actually a three-step process. Saponification occurs first as the reaction medium is heated; this is followed by a two-step elimination of 2 mole equivalents of hydrogen bromide. In aqueous dehydrobromination the saponification is effectively complete by the time the reaction has reached 120C. At this point the reaction medium is homogeneous. The first dehydrobromination occurs readily at 160C, as shown in Table I, whereas the second dehydrobromination is slow at this temperature. This condition would explain why Khan (7) had difficulty in reproducing Adkins' (1) work. At the refluxing temperature of the *n*-amyl alcohol solution used by Adkins, the second dehydrobromination did not readily occur. At a temperature of 180C, the second dehydrobromination occurs readily, and the reaction goes to completion in less than 5 hr.

Recovery of crude stearolic acid from aqueous media is accomplished by cooling the reaction mixture and separating the soap cake from the liquor. The soap is then dissolved in water and filtered to remove the carbon formed during the reaction. After acidification, the precipitated crude stearolic acid is recovered by filtration. This simple recovery procedure should be readily adaptable to a commercial process.

One disadvantage of aqueous dehydrobromination for laboratory use is that a pressure vessel is needed. This problem is overcome by use of 30% KOH in ethylene glycol as the dehydrobrominating reagent. Since dry ethylene glycol boils at 198C, the reaction goes to completion in less than 4 hr. The crude stearolic acid is recovered by adding an equal volume of water to the reaction, neutralizing, and extracting with PE.

During dehydrobromination side reactions are minimal. Samples esterified and analyzed by gas-liquid chromatography (GLC) show several very small unidentified peaks, some of which are removed upon distillation. Ultraviolet absorption indicates diene, triene, and tetraene conjugation in small amounts and very little, if any, allene absorption. Carbon and polymeric materials are also formed during the reaction. They and the conjugated compounds most likely come from the linoleate present in olive oil. This statement is compatible with the observation that after bromination, dehydrobromination, esterification, and vacuum distillation, 89% of the original oleate is recovered as stearolate while weight recovery is only 83%. Evidently, there is a selective removal of linoleic during dehydrobromination.

Purification of the crude stearolic acid from either of the preceding dehydrobromination procedures can be accomplished by following either Khan's (8) or Adkins' (1) crystallization procedures. These procedures have the disadvantage that much stearolic acid is lost. However, after esterification and distilla-

TABLE II
Countercurrent Distribution of Crude Stearolate by Argentation

Fraction	Combined transfers	Weight (%)	Composition (%)			
			Stearolate	Diene	Saturates	Other
Crude	.....	.....	78.7	3.2	14.1	4.0
A	210–259	17.8	.....	18.7	72.8	8.6
B	260–299	4.0	.....	.....	.....	....
C	300–319	22.0	97.8	1.5	.....	0.7
D	320–369	50.7	99.1	.....	.....	0.9
E	370–429	3.3	86.3	.....	6.2	7.5
F	430–588	2.2	13.1	.....	.....	86.9

tion, CCD can be used to purify the crude stearolate with minimal loss of product.

Either an argentation solvent system of *n*-hexane and 0.2 N silver nitrate in 90% aqueous methanol or an N-hexane and acetronitrile solvent system can be used for the purification of methyl stearolate by CCD. Fig. 1 shows the distribution of a crude stearolate sample from olive oil by the argentation system, and Table II gives the GLC analysis of the combined transfers. The saturated materials, palmitate and stearate, are well separated from the stearolate peak. Conjugated dienes contaminate the foreside of the stearolate peak, but transfer combinations can be made so that +99% methyl stearolate can be recovered. Other impurities, such as unreacted oleate from incomplete bromination, are found in Region A, and highly conjugated compounds in Regions E and F. The *n*-hexane and acetonitrile solvent system gives a different distribution curve (Fig. 2). Table III lists the analysis of the combined transfers. Stearate is the first to elute (Region A), followed by palmitate and unreacted oleate. Conjugated dienes again contaminate the foreside of the stearolate peak, but combinations can be made so as to recover a fraction which is +98% stearolate and contains 87% of the stearolate in the crude sample. This represents a yield of 77.5% based upon the oleate in the original oil. This yield is twice that reported by Khan (8) when olive oil was the starting material.

Table IV gives the partition coefficients for stearolate and other fatty esters present in the crude stearolate. As can be seen from Table IV and Figs. 1 and 2, either solvent system can be used to purify the methyl stearolate; however, conjugated dienes are not well separated by either system. If a purer sample than that obtained from CCD is desired, a simple crystallization from ethanol will produce +99.5% stearolate.

Methyl stearolate prepared from olive oil, with ethylene glycol as the dehydrobrominating solvent and hexane-acetonitrile as the solvent system for purification, had a melting point of 2.8C (determined by differential thermal analysis) and a refractive index at 26.0C of 1.4542. This refractive index agrees with Khan's reported value of 1.4545 (9). Since ozonolysis of the methyl stearolate produced only the expected C_9 fragments, no significant amounts of

TABLE III
Countercurrent Distribution of Crude Stearolate with Hexane/Acetonitrile

Fraction	Combined transfers	Weight (%)	Composition (%)			
			Stearolate	Diene	Saturates	Other
Crude	.....	.....	78.7	3.2	14.1	4.0
A	230–289	3.4	.....	.....	100.0	.....
B	290–339	13.1	.....	.....	87.5	12.5
C	340–419	6.2	56.4	34.4	9.1	.....
D	420–499	69.7	98.1	1.2	.....	.....
E	500–619	7.6	90.1	.....	.....	9.9

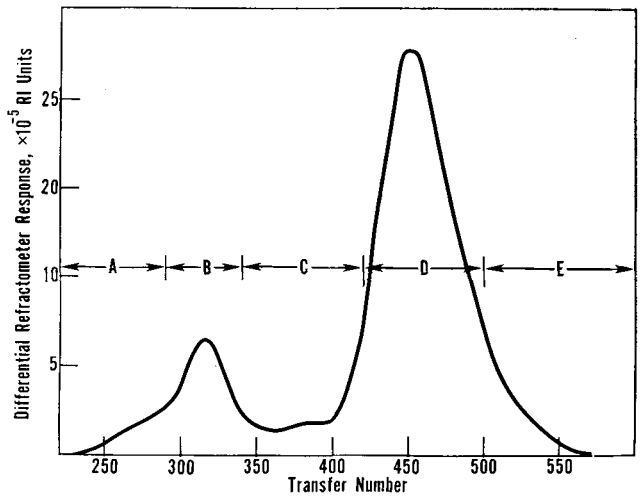


FIG. 2. Countercurrent distribution of crude methyl stearolate from olive oil with 10 ml of *n*-hexane and 40 ml of acetonitrile as the solvent system.

any positional isomers were indicated. Stearolic acid made by saponifying the methyl ester had a melting point of 45.8C. Reported values vary from 45.3 to 47.0C (1,2,7,8,9).

Recommended Procedures

A possible industrial procedure would consist of three unit operations carried out in a glass-lined autoclave equipped for heating, cooling, stirring, and phase separating. Bromination of a high-oleic oil would be carried out directly in the oil or by the patented process of Bornfleth (3), in which a water-hexane solvent system is used. This step would be followed by dehydrobromination with 30% aqueous KOH at 180C under pressure. The soap cake which forms on cooling could be separated by draining off the aqueous liquor. Upon neutralizing the soap cake, crude stearolic acid would precipitate. With olive oil as starting material; this crude final product upon drying would be about 80% stearolic acid. The by-product KBr could be recovered or could be used to generate bromine and KOH by electrolysis for recycling in the process.

The recommended laboratory procedure would consist of brominating an oleic acid oil in a nonreactive solvent, followed by solvent removal and dehydrobromination with 30% KOH in ethylene glycol. Upon cooling and acidifying the cake, the crude stearolic acid is extracted with petroleum ether. After this product is esterified and distilled in vacuum, +99% pure methyl stearolate is obtained by CCD, crystallization, or both, at an 80% yield.

In both laboratory and large-scale procedures, commercially available olive oil—and in the future high-oleic safflower oil (6)—without purification can serve as the starting material. A minimal number of unit operations are involved and these can be carried

TABLE IV
Partition Coefficients for Methyl Esters of Fatty Acids

Compound	Hexane/ Acetonitrile	Hexane/0.2 N $AgNO_3$
Stearolate	3.2	6.9
Linolenate	2.4	2.1
Conjugated diene	4.3	6.2
Linoleate	4.3	5.3
Oleate	7.9	10.5
Stearate	12.0	17.0
Palmitate	8.9	17.0

out industrially in a single autoclave reactor. Purification steps, if required, need be applied only to the products and not to the starting materials. The simplicity of the laboratory procedure commends it for immediate use, and the suggested industrial steps can be investigated more fully as the need for stearolic acid as a chemical intermediate develops.

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