Acetylenic Compounds. II.[1] Preparation and Properties of Stearolic Acid and the Related Substances[2]

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IN CONTINUATION of the previous studies (1, 2) stearolic acid was prepared in larger quantities by employing at different steps procedures of separation by means of urea inclusion compounds. Brominated derivatives of natural fatty acids do not form urea inclusion compounds (3, 4). It might then be feasible to remove saturated acids from the brominated derivatives of the C_{18}-monoethenoic acids in natural sources, which are then dehydrobrominated to yield stearolic acid.

Attempts to separate stearolic acid from the crude reaction mixtures containing palmitic and stearic acids, polymers, and other secondary reaction products were quite successful. This made possible the preparation of the acetylenic acid directly from the natural acids. The degree of separation of stearolic acid from a standard mixture of stearolic and oleic acid was also measured.

The dehydrobromination of 9,10-dibromostearic acid by alcohol KOH, as well as of 13,14-dibromobehenic, tetrabromostearic, and hexabromostearic acids by sodamide in liquid ammonia, were unsuccessful. The presence of bromine in the reaction products shed some light on the dehydrobromination processes.

It was very interesting to debrominate dibromooleic acid (1) to stearolic acid, which also resisted any reduction by sodium in liquid ammonia. However the debromination and reduction of 3,4-dibromohexene and only reduction of 3, hexyne under similar conditions to *trans,* 3-hexene indicated that the vinylic dibromides on debromination form acetylenic derivatives which may undergo reductive hydrogenation.

Experimental

Preparation of 9,10-dibromostearic and stearolic acid. The following acids were brominated in a 30% petroleum ether solution below 0° with excess bromine: a) olive oil acids, I.N. (Iodine Number) 76.2, containing less than 1.0% linoleic acid, which were obtained by the method of Swern and Parker (5); b) crude olive oil acids; c) lard acids; d) cottonseed and corn oil acids; and e) soyabean oil acids. The tetrabromostearic acids from each of the above solutions were removed by crystallization as far as practicable, then thoroughly washed with water until free of acid, and dried over anhydrous sodium sulfate. After evaporation of the solvent the residue (4,500 g.) was slowly added to 5 liters of boiling methanol containing 2,000 g. of urea. The mixture was stirred vigorously and allowed to cool overnight. The crystals were filtered and washed with a mixed solvent of ethyl ether and petroleum ether (1:1). The crystallization processes were repeated by adding 1,000 g. of urea at a time to the boiling filtrates until bromo-acids in the filtrate were free from saturates. The major portion of methyl alcohol in the filtrate was removed by evaporation under vacuum. The precipitated crystals were filtered and washed with ethyl ether. The mixture of filtrate and wash liquid was allowed to settle, and the precipitate was again filtered off. The final filtrate was washed free of alcohol with water and dried. The solution obtained was ready for dehydrobromination. If infrared absorption analysis indicated formation of methyl ester in the residue from this solution, the residue was hydrolyzed to free acids (1).

Stearolic acid was obtained from the dibromides of *a* to *d* by the methods previously described (1, 2) except for the adjustment of the quantity of sodium according to the tetrabromides present. The yields of stearolic acid (M.P., 46.0–46.5°C.); H_2-absorption, 2.0 moles/mole) were as follows: a) 56–64%; b) through e) 44–58%.

Fractionation of Mixtures Containing Stearolic Acid by Urea-Inclusion Compounds. Four batches of dehydrobrominated products (2) from crude olive oil acids (500 g. each) were added to the boiling methyl alcohol (1 gal.) containing 1,000 g. urea. The mixture was vigorously stirred and left overnight. The crystals were removed by filtration. The above process was repeated five more times with the addition, successively, of II 1,000, III 500, IV 1,500, V 1,000, and VI 500 g. of urea to the boiling filtrate. Table I indicates the degree of separation of fatty acids. The same sequence of treatment was used for four batches of reaction products from olive oil acids freed of the saturates. The quantities of urea used were: I 1,500, I 2,000, III 1,500, and IV 1,000 g. Table II shows the results. In the standard mixture, stearolic acid (200 g.) and oleic acid (100 g.) were dissolved in 500-ml. methyl alcohol. The fractions were obtained with, respectively, I 200, II 250, III 200, IV 250, and V 250 g. of urea. The distribution of fatty acids calculated on the basis of hydrogen absorption and iodine number (10) is shown in Table III.

TABLE I

Separation of Stearolic Acid from Crude Reaction Mixtures Containing Palmitic and Stearic Acids

Fractions	Percentage of the original acids	Stearolic acid[a] in percentage of purity	Crystallization from petroleum ether and stearolic acid in percentage of purity
1	7.8	6.0	....
II	11.1	34.7	....
III	9.6	77.4	Four stepwise crystallizations in dilute solution (3–5%) → 100.0
IV	20.7	89.8	
V	14.4	92.6	Two stepwise crystallizations in dilute solution (2–3%) → 100.0
VI	6.9	94.4	

[a] m.p. and H_2-absorption.

Dehydrohalogenation Reactions by Alcoholic Alkali. A batch of 300 g. of methyl oleate, I.N. 87.9, 95–97% pure (1) was treated according to the method of Adkins *et al.* (6). The resulting products contained bromine and failed to yield stearolic acid.

Preparation of Behenolic Acid. Bromination of 35 g. of erucic acid in 250 ml. of absolute ether was carried out below 15°C. The dibromides formed were subjected to dehydrobromination by sodamide in liq-

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[1] Paper I in the series is reference 2.

[2] Presented at the Fall Meeting of the American Oil Chemists' Society, Philadelphia, Pa., Oct. 10–12, 1955.

TABLE II

Separation of Stearolic Acid from Crude Reaction Mixtures Containing Polymers

Fractions	Percentage of the original acids	Stearolic acid in percentage of purity	Color
I	6.7	92.0	None
II	10.4	96.0	None
III	30.6	100.0	Light yellow [a]
IV	12.4	100.0	Light tan [a]

[a] One crystallization from acetone yielded white crystals.

uid ammonia (1). The liquid products contained bromine and yielded no solids.

Dehydrohalogenation of Tetrabromo- and Hexabromo-Stearic Acids. It has been previously (2) shown that the dehydrohalogenation of tetrabromostearic acid is not feasible. However attempts have now been made to dehydrohalogenate tetrabromo- and hexabromo-stearic acids (each as 0.1 mole in 2-liter liquid ammonia, with 0.6 and 0.8 mole of sodium, respectively), using 500 ml. of precooled heptane as solvent. Even then it was not possible to prevent polymerization, which gave polymers containing bromine.

Reduction of Stearolic Acid. Twenty-eight grams of stearolic acid were dissolved in 100 ml. of absolute ether (distilled over sodium) and added to 12 g. of sodium in liquid ammonia, following the procedures of Campbell *et al.* (7). On recovering the reaction products, the stearolic was found unchanged. Twenty-eight grams of stearolic were converted to neutral soap, which was then freed from the solvent, dried under vacuum, and added to the solution of sodium in liquid ammonia. Stearolic acid was again found unchanged. Stearolic acid was then converted to the viscous, liquid 9,10-dibromo-oleic acid (1) and added as a solution in absolute ether to sodium (twice the usual amounts) in liquid ammonia. On recovery of the reaction products, stearolic acid (m.p., 46.0–46.5° C.; H_2-absorption, 2 moles/mole; infrared absorption, no *trans* isomer) was obtained almost quantitatively.

Preparation and Reduction of 3,4-Dibromohexene. 3-Hexyne (b.p., 81.1–81.4° and N^{20}, 1.4112) was brominated in Yasuda's reaction mixture (8) with some modifications. Two moles (164 g.) of the substances plus 250 ml. of acetic acid were placed in a 5-liter, 3-necked flask and kept cooled below 15°C. 500 ml. of Yasuda's solution were added to the flask and stirred rapidly. 500 ml. more of the solution were added slowly in drops from one separatory funnel, and the remainder of the total bromine required (325 g., *Ca.* 102 ml.) from another. When the addition was complete, the mixture was stirred for one additional hour. Half of the acetic acid was neutralized slowly with dilute KOH solution; the mixture was diluted to twice its volume and extracted with ethyl ether; the extract was washed and dried. On removal of ether and unreacted 3, hexyne under suction, the bromo-derivatives were obtained; these were then added, with 250 ml. of absolute ethyl ether, very slowly to sodium in liquid ammonia. The debromination procedure was modified as follows. The gas outlet was allowed to pass through two traps, one in the freezing mixture of ice and salt, and the other in pure chipped ice. On completion of the reaction, ammonium chloride was added very carefully. The first attempt was unsuccessful because of too rapid addition of ammonium chloride and lack of proper manipulation. The second time some organic substance was recovered from the traps and the reaction flask and was redistilled in a small fractionating column. The major product was found to be *trans,* 3-hexene (b.p., 67.4–67.6°C.; N^{20}, 1.3938). The presence of the isolated *trans*-double bond was also verified by the infrared absorption curves.

Reduction of 3, Hexyne. This was carried out according to the method of Campbell *et al.* (7) with all necessary precautions as mentioned in the foregoing section. The product was identified as *trans,* 3-hexene.

Infrared absorption analysis was carried out by a Perkin-Elmer Instrument, Model 21. The tested wavelengths were: 2.0–6.0 μ and 8.0–14.0 μ (10.36 μ in particular for isolated *trans* double bond).

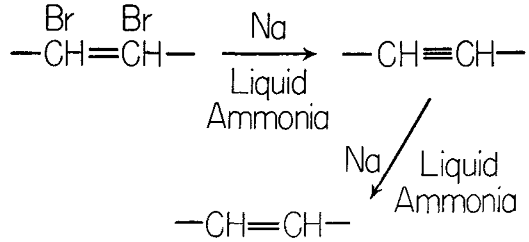

FIG. 1.

Discussion

The procedures for isolation of oleic and dibromostearic acid by means of urea-inclusion compounds may be used as general guides for the possible applications to various natural and commercial materials available. Ingenuity in employing similar procedures may help in preparing stearolic acid easily. Separation of stearolic acid from other fatty acids and polymers further promises to simplify its preparation. Moreover the tetrabromides obtained as side-products may be used for preparation of linoleic acid (9).

Hydrobromic acid, formed during the bromination processes in the open air, may be responsible for the esterification of fatty acids in methyl alcohol used for urea-inclusion compounds. Precautions should be taken to prevent such formation of HBr by using a closed system or by other means.

The presence of bromine in products obtained from dehydrohalogenation reactions of alcoholic KOH with dibromostearic acid, and of sodamide in liquid ammonia with dibromobehenic acid, indicates that the two reagents are ineffective in pulling off both molecules of HBr. The bromine left in the polymer molecules may support the stepwise dehydrobromination as postulated in previous publications (1, 2). This may also suggest that polymerization occurs during

TABLE III

Separation of Stearolic Acid from a Standard Mixture of Stearolic and Oleic Acids (2:1) by Urea-Inclusion Compounds

Fractions	Percentage of the original acids	Percentage of stearolic acid in the fractions
I	24.6	95.6
II	26.9	88.7
III	18.1	58.4
IV	20.4	20.6
V	8.7	3.8

[a] H_2-absorption and iodine number.

stepwise processes in which all bromine atoms of the polybromides are not eliminated.

Apparently stearolic acid cannot be reduced by sodium in liquid ammonia possibly because of its low solubility. The liberation of stearolic acid from dibromo-oleic acid confirmed this idea. The other acetylenic compounds have been reduced by sodium in liquid ammonia (7). Furthermore the fact that 3,4-dibromohexene and 3, hexyne both yield *trans*, 3-hexene, gives some clues to the steps in the sodium debromination and reduction in liquid ammonia. The 1,2-dibromo ethylene structure is debrominated with sodium in liquid ammonia to the acetylenic bond, which immediately is reduced by the sodium and liquid ammonia to the ethylenic bond. The insolubility of stearolic acid in liquid ammonia possibly prevents the reduction processes which proceed smoothly in the cases of 3, hexyne and its derivative. However, if the electron addition to the triple bond and the subsequent repulsion of alkyl groups are necessary for reduction of the triple bond as postulated by Greenlee and Fernelius (11), either electron addition will not be possible because of the insolubility mentioned, or the repulsion processes cannot occur in the long chain alkyl groups.

Summary

1. 9,10-Dibromostearic acid has been prepared in different grades of purity through urea-inclusion compounds from natural sources of fatty acids. This facilitated preparation of stearolic acid.

2. The degree of separation of stearolic acid from other fatty acids and polymers by means of urea-inclusion compounds was ascertained.

3. The attempts at preparation of behenolic acid by dehydrobromination of 13,14-dibromobehenic acid ended in failure.

4. Stearolic acid could not be reduced by sodium in liquid ammonia. Debromination of 9,10-dibromooleic acid yielded stearolic acid whereas reduction of 3, hexyne and debromination of 3,4-dibromohexene resulted in the formation of *trans*, 3-hexene. Hence a reaction sequence involving debromination of vinylic dibromides and subsequent reductive hydrogenation has been proposed.

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Direct Potentiometric Titration of Oxirane Oxygen by Hydrogen Chloride-Acetic Acid[1]

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WITH THE ADVENT OF epoxy plasticizers, epoxy resins, and the use of epoxy compounds as intermediates and reagents a variety of methods have been developed for the determination of oxirane oxygen. All of these methods are indirect and can be classified under the following groups:

a) hydrochlorination in ethers, pyridine, water, or alcohols (2, 4, 7, 9, 11).
b) reaction with amines (6, 5, 8).
c) hydration of epoxy groups (8).
d) reaction with sodium sulfite, sodium thiosulfate, alkali derivatives of thiols, hydrogen sulfide, and alkali hydrosulfides (3, 10, 12).
e) reaction with anilinium hydrochloride in glacial acetic acid and back titration of the liberated aniline (1).

The methods that have found the widest applicability are those employing hydrochlorination in ethyl ether (9), pyridine (2), or dioxane (7). The long reaction time (3 hrs.) and the inconsistency of results obtained by the ethyl ether-hydrochloric acid method, especially during the summer months, are well known. The special purification of dioxane required and the weak end-point make the dioxane hydrochloric acid method time-consuming and unreliable. The pyridine hydrochloride reagent requires a carefully controlled reflux reaction time. The odor of pyridine makes its use for routine analysis objectionable.

The present method[2] was developed in order to overcome the difficulties of the existing methods and to provide a method which is more consistent, reliable, accurate, and direct.

The acetic acid-hydrochloric acid method is based on the fact that compounds which exhibit weak basic properties in aqueous solutions can be titrated readily in glacial acetic acid. Acetic acid is an acidic solvent and a poor proton acceptor. Therefore only those substances which are the strong acids in water, such as perchloric, sulfuric, hydrobromic, and hydrochloric acids, exhibit marked acidic character in acetic acid. Preliminary investigations indicated that perchloric acid and sulfuric acid gave side reactions when employed for titration of epoxy compounds in glacial acetic acid. Hydrochloric acid and hydrobromic acid were acceptable. The present paper deals with the titration of oxirane oxygen by hydrochloric acid-acetic acid. A subsequent paper will detail work done with a hydrobromic acid-acetic acid reagent.

Experimental

A. Reagents and Apparatus

1. A Beckman pH meter Model H-2 with a capillary calomel electrode and a glass electrode, red label 8990-80.
2. Reservoir Buret Karl Fisher type with long-angled tip and

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[1] Paper presented at the 29th Fall Meeting of the American Oil Chemists' Society, Philadelphia, Pa., Oct. 10, 1955.

[2] The possibility of using hydrogen chloride in glacial acetic acid was first suggested by V. C. Mehlenbacher of Swift and Company at a meeting of the A.O.C.S. Oxirane Oxygen Analytical subcommittee. Work in Swift laboratories, using indicators, had given poor endpoints and erratic results.