



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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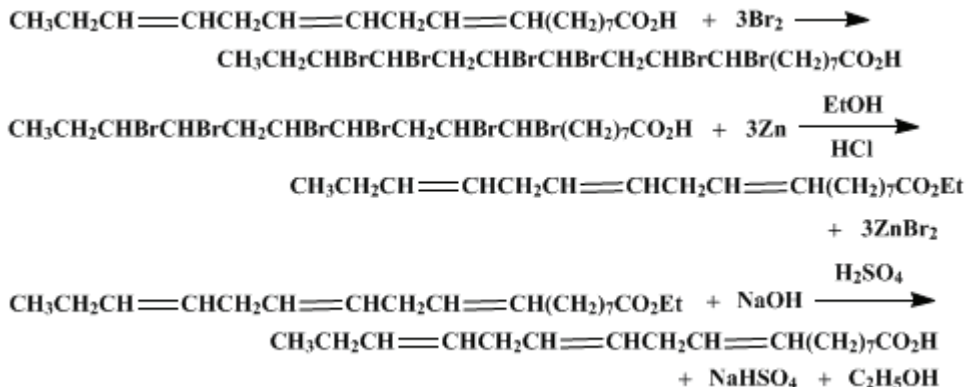
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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LINOLENIC ACID



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1. Procedure

A. *Fatty acids*. The procedure outlined for [linoleic acid](#) (p. 526) is followed, omitting [\(Note 3\)](#) and [\(Note 4\)](#). Linseed oil is used as the raw material.

B. *Hexabromostearic acid*. In a 4-l. beaker equipped with a mechanical stirrer [\(Note 1\)](#), 90–95 g. of the fatty acids is dissolved in 2.5 l. of [ethyl ether](#), and the solution is chilled to 0–10°. Then, with stirring, 35 ml. of [bromine](#) [\(Note 2\)](#) and [\(Note 3\)](#) is introduced slowly, from a dropping funnel [\(Note 4\)](#), at such a rate that the temperature does not exceed 20°; about 50 minutes is usually required. The solution, which must contain an excess of [bromine](#) (deep red color), is allowed to stand in an ice bath at 0–10° overnight. The excess [bromine](#) is removed by addition of a small amount of [amylene](#), and then the white precipitate is collected with suction on a 12.5-cm. Büchner funnel and is washed with 200 ml. of [ethyl ether](#). The hexabromide is thoroughly stirred with 300 ml. of [ethyl ether](#) in a 600-ml. beaker and is filtered as before. The yield is 20–22 g. of gray-white [hexabromostearic acid](#) [\(Note 5\)](#). It is recommended that 100 g. of the crude hexabromide [\(Note 6\)](#) be accumulated before proceeding to the next step.

In a 1-l. beaker 100 g. of crude [hexabromostearic acid](#) is heated to 70–80° with 600 ml. of [dioxane](#) [\(Note 7\)](#). The mixture is filtered, and the filtrate is set aside at 15–20° for several hours or preferably overnight. The precipitate is collected on a Büchner funnel with gentle suction and is washed thoroughly on the funnel with several 300-ml. portions of [ethyl ether](#). The hexabromide is then transferred to a glass plate and spread out with a glass spatula to dry in the air. The fine snow-white crystals weigh 80 g. and melt at 181.5–181.9° [\(Note 8\)](#).

C. *Ethyl linolenate*. In a 1-l. Erlenmeyer flask 80 g. of the pure hexabromide is dissolved in 190 ml. of absolute [ethanol](#), and 40 g. of granulated [zinc](#) (20 mesh) is added. The mixture is refluxed for 1 hour, at the end of which time the solution should be clear. About 10 g. of [zinc](#) dust is added, refluxing is continued for a short time, and then 10 ml. of 4 *N* [ethanol-hydrochloric acid](#) (p. 530) is added. Refluxing is continued for 6 hours, and during this time 5 ml. of the ethanolic [hydrochloric acid](#) is added every 30 minutes. At the end of 6 hours, the solution is removed from the unchanged [zinc](#) by decantation into another flask, and the [zinc](#) is washed with 15 ml. of absolute [ethanol](#) to complete the transfer of the solution. A 10-ml. portion of ethanolic [hydrochloric acid](#) is added, and the solution is refluxed for a period of 3 hours, with addition of 5-ml. portions of ethanolic [hydrochloric acid](#) at 30-minute intervals. The mixture is poured into 500 ml. of hot saturated brine solution in a 1-l. separatory funnel, and the crude ester is allowed to settle for 10–20 minutes. The brine is removed, and the ester is washed [\(Note 9\)](#) at room temperature with 500 ml. of 0.5% [sodium carbonate](#) solution. The rather stable emulsion is broken by centrifuging the mixture for 5 minutes at 3300 r.p.m. The ester and any remaining emulsion

are washed with 150 ml. of warm water, and the emulsion is broken by centrifuging. Washing (Note 10) is continued until the wash water is neutral to methyl orange. The neutral ester is distilled under reduced pressure. It boils at 174°/2.5 mm. and 198°/6.5 mm.

D. *Linolenic acid*. The ester is dissolved in 400 ml. of a 5% ethanolic solution of sodium hydroxide in a 1-l. beaker, and the solution is allowed to stand overnight at room temperature. The resulting jelly is dissolved in 400 ml. of warm water, and a slow stream of carbon dioxide is introduced beneath the surface of the liquid while it is acidified with 50 ml. of dilute sulfuric acid (1:1 by volume). The stream of carbon dioxide is maintained throughout the subsequent operations. The linolenic acid rises to the surface as a clear layer, which is washed once with hot water. The acid is dried over anhydrous sodium sulfate and is preserved under carbon dioxide. The yield of acid is 22–24 g., and the product has a melting point of –17° to –16° (Note 11).

2. Notes

1. In order to guard against fire hazard it is advisable to use hand stirring when proper safety equipment is not available.
2. Care must be observed that the stopcock does not slip out of place.
3. The weight of bromine is independent of the amount (per cent) of linolenic acid in the sample, but it varies with the iodine value. For the purposes of this experiment the amount of bromine (grams) may be calculated as 0.7 times the iodine value of the oil. This allows an excess of 10–11%.
4. The tip of the dropping funnel should be just above the fatty acid solution in order to avoid plugging the exit.
5. The yield is based on a linseed oil containing approximately 45% of linolenic acid. Because of the formation of stereoisomers, only 25% of the bromoacid is precipitated in the solid form. By using water-white distilled linseed fatty acids, obtained from Archer-Daniels-Midland Company, Minneapolis, Minnesota, the yield of solid bromoacid may be increased to 48–53 g.
6. The theoretical yield of the ethyl ester from 20 g. of pure hexabromide is 8 g. Losses through recrystallization, distillation, etc., amount to approximately 50%; hence the actual yield is about 4 g. of ester.
7. The by-product, insoluble in dioxane, is heptabromostearic acid. If the solution is yellow at this point, a small amount of decolorizing charcoal should be added.
8. The melting point varies with the rate of heating. Any uniform method of taking the melting point may be adopted. It has been found convenient to insert the capillary tube in the bath when the temperature is 5° below the expected melting point, and then to raise the temperature 1° per minute.
9. The ester contains about 0.5% of free fatty acid, and for some purposes this is not objectionable, particularly if the acid itself is desired. It is recommended, therefore, that this step be omitted where possible, since the yields, particularly from small batches, may be as low as 80% of the crude ester used. In the absence of an alkaline wash centrifuging is not necessary, as water alone causes no emulsions to form.
10. Usually three washings are sufficient.
11. The ester is much more stable toward oxidation than the acid; it is recommended that the material be stored as the ester, and that the acid be prepared only for immediate use. The acid oxidizes to some extent under the best of conditions and, unlike the ester, cannot be distilled without some decomposition. It is for this reason that the constants are determined on the ester rather than on the acid.

3. Discussion

Linolenic acid is always obtained from natural sources, chiefly from the oils of various seeds, such as hemp seed,¹ walnut,² poppy seed,² cotton seed,² and, best of all, linseed.^{3,4} The crude acid has been purified via the solid hexabromide, either directly,^{5,6,7} or by the hydrolysis of the methyl or ethyl ester, obtained by simultaneous debromination and esterification of hexabromostearic acid.^{5,8} The method described above is a modification^{9,10} of the procedure of Rollett.⁸ The acid has also been obtained from soy oil and has been purified via the hydroxamic acid.¹¹

References and Notes

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 2. Hazura and Grüssner, *Monatsh.*, **9**, 204 (1888).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

brine

ethanolic solution of sodium hydroxide

hydroxamic acid

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ethyl ether (60-29-7)

sodium carbonate (497-19-8)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

carbon dioxide (124-38-9)

zinc (7440-66-6)

dioxane (123-91-1)

amylene

Linoleic acid (60-33-3)

Linolenic acid (463-40-1)

Hexabromostearic acid

heptabromostearic acid

methyl orange (547-58-0)

Ethyl linolenate (1191-41-9)

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