



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

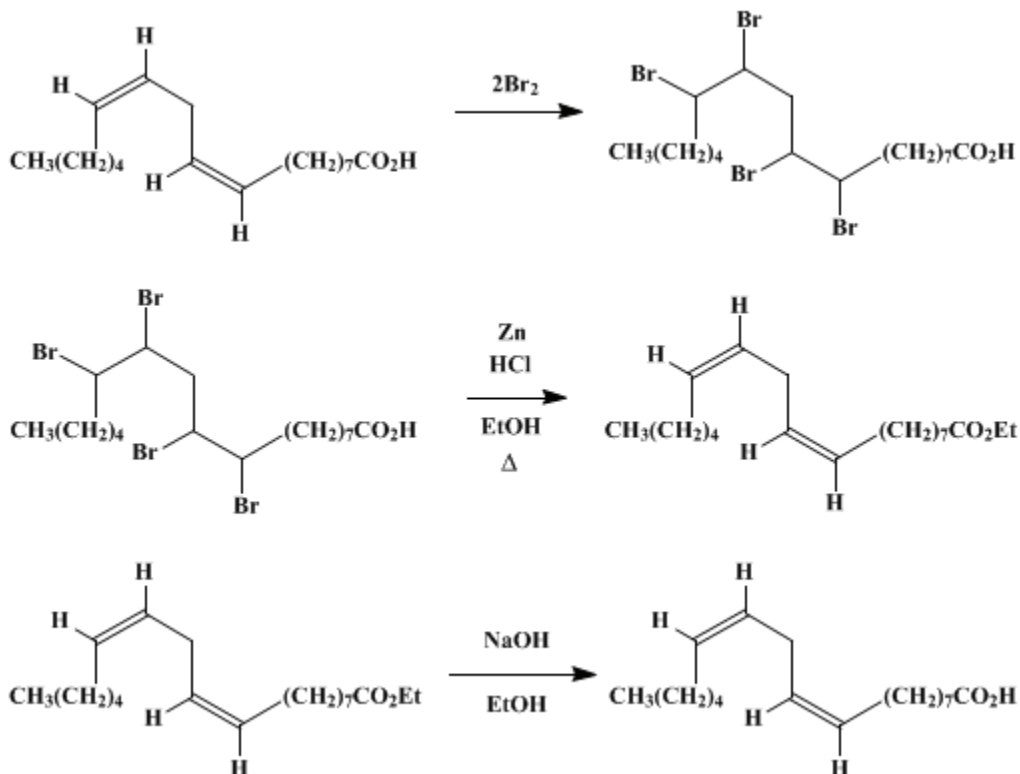
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 3, p.526 (1955); Vol. 22, p.75 (1942).*

## LINOLEIC ACID



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### 1. Procedure

A. *Fatty acids.* In a 1-l. Erlenmeyer flask are placed 250 ml. of dynamite-grade glycerin (Note 1) and 40 g. (0.71 mole) of potassium hydroxide. The mixture is heated to 120–140° and is shaken by hand until the alkali is dissolved. To the hot solution there is added, in one portion (Note 2), 110 ml. (100 g., 0.11 mole) of sunflower-seed oil (Note 3) and (Note 4) which has been preheated to 110–115°. The hot solution is swirled vigorously until saponification is complete (Note 5). This is indicated by the formation of a permanent lather. After the mixture has cooled somewhat, 150 ml. of sulfuric acid (25% by volume) is added cautiously (Note 6) while the flask is swirled. Then 200 ml. of hot water is added, and, if necessary, the mixture is heated until the layer of fatty acid is clear. The water layer is removed, the acid layer is washed with two 500-ml. portions of hot water, and then it is filtered with the aid of suction through a large Hirsch funnel which is heated by a steam or hot-water jacket. The acids (90–95 g.) (Note 7) are dried thoroughly by heating them rapidly to 130°, with stirring.

B. *Tetrabromostearic acid.* In a 4-l. beaker equipped with a mechanical stirrer the above fatty acids are dissolved in 2 l. of petroleum ether (Note 8), and the solution is chilled to 0–10°. After 20–25 minutes, the solution deposits about 10 g. of solid saturated fatty acids, which are removed by rapid filtration with gentle suction. The filtrate is transferred to the 4-l. beaker and cooled to 0–10°. Then, with stirring, 30.7 ml. (90 g., 0.56 mole) of bromine (Note 9) is slowly introduced from a dropping funnel (Note 10). The bromine is added at such a rate that the temperature remains between 10° and 15°; about 20 minutes is usually required. Tetrabromostearic acid begins to separate toward the end of the addition. The solution, which should contain a slight excess of bromine (reddish color), is allowed to remain in the ice bath for 15–20 minutes (Note 11). The precipitate settles rapidly, and a large portion of the liquid is removed by decantation, after which the precipitate is finally collected with suction on a 12.5-cm. Büchner funnel and is washed with 200 ml. of petroleum ether. The solid is then thoroughly

stirred with 300 ml. of petroleum ether (Note 12) in a 600-ml. beaker and is filtered as before. The gray-white tetrabromide, after being dried at 50°, is transferred to a 2-l. beaker and dissolved in 90–100 ml. of hot ethylene dichloride (Note 13). The solution is filtered through filter paper and allowed to crystallize at room temperature. The solid is removed by filtration and is washed on the funnel with 200 ml. of fresh petroleum ether. The tetrabromide is transferred to a glass plate and is worked to a powder (Note 14) with a spatula. The needle-shaped crystals are snow-white, with a silvery sheen, and have a melting point of 114.7–115.2°. The yield (Note 15) is 35–40 g. (32–36%) (Note 16). The product should be stored in brown screw-top bottles and kept away from sunlight.

C. *Ethyl linoleate*. In a 300-ml. Erlenmeyer flask are placed 26–30 g. of recrystallized tetrabromostearic acid, 85 ml. of absolute ethanol, and 30 g. of granulated zinc (20 mesh). This mixture is warmed gently until the debromination reaction begins. Since the reaction is exothermic, it is usually necessary to moderate it from time to time by dipping the flask into a basin of cold water. The vigorous reaction subsides in about 5 minutes, after which the flask is fitted with a reflux condenser and the mixture is refluxed for 30 minutes. In order to esterify the linoleic acid, 10 ml. of a 4 N solution of hydrochloric acid in ethanol (Note 17) is poured into the refluxing mixture through the top of the condenser, and successive 5-ml. portions are then added every 30 minutes for 2 hours. At the end of this time the solution is removed from the unchanged zinc by decantation into another flask. The zinc is washed with 15 ml. of absolute ethanol to complete the transfer of the solution. A 10-ml. portion of 4 N ethanolic hydrochloric acid is added and the solution is refluxed for an hour, with addition of a second 10-ml. portion of ethanolic acid after 30 minutes. The mixture is poured into 300 ml. of hot, saturated brine solution in a 500-ml. separatory funnel, and the crude ester is allowed to settle for 10–20 minutes. The brine layer is removed, and the ester is washed (Note 18) at room temperature with 300 ml. of 0.5% sodium carbonate solution. The rather stable emulsion is broken by centrifuging the solution, in 100-ml. tubes, for 5 minutes at 3300 r.p.m. The ester and any remaining emulsion are washed with 80 ml. of warm water, and the emulsion is again broken by centrifuging. Washing is continued (Note 19) until the wash water is neutral to methyl orange. The neutral ester is then transferred to a 50-ml. distilling flask and is distilled under reduced pressure; boiling point, 175°/2.5 mm., 193°/6 mm. The product is water-white (Note 20), gives a negative Beilstein test, has an iodine value (Wijs, 30-minute exposure) of 162.3–162.5, an  $n_D^{48}$  of 1.4489, and a true specific gravity of 0.8846 at 15.5/4°. The yield (Note 15) is 12–15 g.

D. *Linoleic acid*. The ester is dissolved in 200 ml. of a 5% ethanolic (Note 21) solution of sodium hydroxide in a 400-ml. beaker and is allowed to saponify overnight at room temperature. The resulting jelly is dissolved in 200 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 linoleic acid rises to the surface as a clear layer. The water layer is siphoned off; the acid is washed once with hot water and then dried over anhydrous sodium sulfate and preserved under carbon dioxide. The yield is 10–12 g. of material having a melting point of –8° to –9° (Note 22).

## 2. Notes

1. Dynamite-grade glycerin is specified, because of its high glycerol content (99 plus per cent). Water interferes with the ease of saponification.
2. The oil must not be allowed to run down the side of the flask, as this interferes with complete saponification.
3. The following oils are recommended in decreasing order of preference, the numbers in parentheses indicating the approximate linoleic acid content: sunflower-seed oil (60), poppy-seed oil (60), cotton-seed oil (45).
4. The sample used must have a negative hexabromide test, indicating the absence of acids more highly unsaturated than linoleic. The test is carried out as follows: 2 ml. of the oil and 25 ml. of a 4:1 ethyl ether-glacial acetic acid mixture are chilled to 0° for 15–20 minutes; the mixture is filtered if it is not clear. To this solution is added sufficient bromine to give a deep red color, and the whole is allowed to stand for 15 minutes. The absence of a precipitate constitutes a negative test.
5. Usually 4–6 minutes of vigorous swirling is sufficient, but it may be necessary to reheat the mixture to 150° if difficulty is encountered. Saponification, once started, proceeds to completion within a few

seconds. The emulsion thickens to a viscous paste which is transformed into a clear, limpid solution on continued swirling.

6. By adding the acid to the *hot* solution, with vigorous agitation, delay in clearing the fatty acid layer is avoided.

7. When large quantities of the fatty acids are desired, the following method is more economical: In a 5-l. round-bottomed flask, fitted with a mechanical stirrer and a reflux condenser, are placed 1.5 l. of [methanol](#) and 350 g. of [potassium hydroxide](#). After solution is complete, 1.1 l. (1 kg.) of cotton-seed oil is added. The solution is stirred and refluxed for 1–2 hours, and then the [methanol](#) is removed by distillation. To the residue are added 1 l. of water and (slowly) 1.5 l. of cold 20% [sulfuric acid](#). The fatty acid layer is separated from the water layer, washed with two 1.5-l. portions of hot water, and then filtered with the aid of a hot-water funnel. The acids are dried as described above. The yield is 950–975 g. of crude acids.

8. The petroleum ether used throughout had a boiling range of 40–60°.

9. The weight of [bromine](#) is independent of the amount (per cent) of [linoleic acid](#) in the sample, but it varies with the iodine value.<sup>1</sup> For the purpose of this preparation, 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%.

10. The tip of the dropping funnel should be just above the fatty acid solution.

11. [Tetrabromostearic acid](#) has a decided tendency to form a supersaturated solution in petroleum ether.

12. The solubility of the tetrabromide<sup>2</sup> is about 2–3 g. per l. of petroleum ether at room temperature, hence there is little danger of losing appreciable quantities by solution during the washing.

13. As an alternative but less satisfactory method of purification, the crude tetrabromide may be dissolved in 800 ml. of [ethyl ether](#), filtered, and reprecipitated by stirring the solution into 800 ml. of petroleum ether. This solution is cooled below 20° and allowed to stand overnight. Ninety per cent of the precipitate will be deposited in 2 hours. The solid is removed by filtration and is washed on the funnel as described above.

14. The ease with which the product dries and powders is an indication of its purity. Usually the material falls apart to a fine white powder at the mere touch of the spatula. A glass spatula should be used in the transfer of the crude material before the recrystallization.

15. These figures are based on the use of sunflower-seed oil containing 57% [linoleic acid](#). With other oils, the yield will be proportionally larger or smaller, depending on the analysis of the oil. Approximate values for three oils may be calculated from the values given in Note 3 above. The yield from cotton-seed oil is 26–30 g. The checkers have brominated about nine times the amounts stated in these directions and have obtained proportionate yields.

16. Two isomers, a solid and a liquid, are formed during the bromination.

17. The 4 *N* ethanolic [hydrochloric acid](#) is prepared by passing dry [hydrogen chloride](#) gas into slightly warmed absolute [ethanol](#) until the calculated increase in weight is obtained.

18. 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 the 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.

19. Usually three washings are sufficient.

20. A small amount of decolorizing carbon may be added before distillation, but it is usually unnecessary and is to be avoided if possible, for it is likely to cause priming in the still.

21. Ordinary 95% denatured [ethanol](#) is satisfactory here.

22. 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

[Ethyl linoleate](#) is prepared by debromination of the tetrabromide by action of [zinc](#), or nascent [hydrogen](#) from [zinc](#) and glacial [acetic acid](#);<sup>3</sup> by [zinc](#) and ethanolic-[hydrochloric acid](#);<sup>2,4</sup> and by [zinc](#) and ethanolic-[sulfuric acid](#).<sup>5</sup> The pure acid can be obtained by saponification of the ester, by hydrolysis of the hydroxamic acid,<sup>6</sup> and directly by the action of [zinc](#) and [pyridine](#) (or [quinoline](#), [aniline](#), [piperidine](#)) on [tetrabromostearic acid](#).<sup>7</sup> It has also been prepared from 1-iodohexadecadiene-7,10 by condensation

with malonic ester and subsequent hydrolysis.<sup>3</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 531](#)

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## References and Notes

1. *Official and Tentative Methods of the American Oil Chemists Society*, revised to Jan. 1, 1941, p. 31, Gillette Publishing Co., 330 S. Wells St., Chicago, Illinois.
  2. McCutcheon, *Can. J. Research*, **B16**, 158–175 (1938).
  3. Baudart, *Peintures, pigments, vernis*, **22**, 375 (1946); [*C. A.*, **41**, 2694 (1947)].
  4. Rollett, *Z. physiol. Chem.*, **63**, 410–421 (1909).
  5. Kimura, *Fettchem. Umschau*, **4**, 78 (1935).
  6. Inoue and Yukawa, *J. Agr. Chem. Soc. Japan*, **17**, 771; *Bull. Agr. Chem. Soc. Japan*, **17**, 89 (1941) [*C. A.*, **36**, 4803 (1942)].
  7. Kaufmann and Mestern, *Ber.*, **69**, 2684 (1936).
  8. Erdmann and Bedford, *Ber.*, **42**, 1324 (1909); Erdmann, Bedford, and Raspe, *Ber.*, **42**, 1334 (1909).
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

petroleum ether

brine

[ethanol \(64-17-5\)](#)

[sulfuric acid \(7664-93-9\)](#)

[hydrogen chloride,](#)  
[hydrochloric acid \(7647-01-0\)](#)

[acetic acid \(64-19-7\)](#)

[methanol \(67-56-1\)](#)

[ethyl ether \(60-29-7\)](#)

[aniline \(62-53-3\)](#)

[hydrogen \(1333-74-0\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[glycerol,](#)

glycerin (56-81-5)  
sodium carbonate (497-19-8)  
bromine (7726-95-6)  
sodium sulfate (7757-82-6)  
ethylene dichloride (107-06-2)  
carbon dioxide (124-38-9)  
pyridine (110-86-1)  
potassium hydroxide (1310-58-3)  
zinc (7440-66-6)  
piperidine (110-89-4)  
Quinoline (91-22-5)  
Linoleic acid (60-33-3)  
Tetrabromostearic acid (18464-04-5)  
Ethyl linoleate (544-35-4)  
1-iodohexadecadiene-7,10  
methyl orange (547-58-0)