



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). 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.605 (1955); Vol. 20, p.67 (1940).

METHYL MYRISTATE AND METHYL PALMITATE AND THE CORRESPONDING ACIDS



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1. Procedure

In a 3-l. round-bottomed flask are placed 500 g. of bayberry wax (Note 1), 600 g. of methanol, and 31 g. of sulfuric acid. Boiling chips are added, and the mixture is refluxed for 48 hours on the steam bath. About half of the methanol is removed by distillation, and 500 ml. of water is added to the remaining mixture. The ester layer is separated and washed several times with water. About 500 g. of crude methyl esters is obtained.

The esters are fractionally distilled through a suitable fractionating column (Note 2). A second fractionation is then made so that each successive fraction is added to the distilling flask after the temperature has reached the upper limit for the fraction being collected. There is obtained 170–190 g. of methyl myristate, b.p. 91–94°/0.5 mm., 112–116°/1 mm., or 157–162°/10 mm., and 170–190 g. methyl palmitate, b.p. 115–118°/0.5 mm., 129–133°/1 mm., or 180–183°/10 mm. (Note 3), (Note 4), (Note 5), and (Note 6).

2. Notes

1. Bayberry wax, also known as myrtle or laurel wax, is obtained from the berries of various species of *Myrica*. The commercial wax, prepared from the berries of *Myrica cerifera*, may be obtained from chemical supply houses for about \$0.60 per pound. The relative proportion of myristin and palmitin in bayberry wax varies somewhat, but these two compounds constitute about 95% of the wax.

2. Several columns are suitable for this separation. The submitters used a three-ball Snyder column 26 cm. in length (similar to No. 28575 of E. H. Sargent, Chicago), sealed to a 500- or 200-ml. modified Claisen flask. The method of operation was essentially that of Simons and Wagner.¹ The column was not electrically heated but was snugly wrapped with asbestos paper. The rate of distillation was about 20 drops per minute, and the reflux ratio 2 or 3 to 1. Flooding of the column must be carefully avoided. The checkers used a modified Widmer column which carried a spiral, 14 cm. long with eleven turns of the helix, contained in a glass tube 12 mm. in internal diameter. A 500-ml. flask was employed for the first fractionation and a 250-ml. one for the refractionation. The column and the oil bath were heated electrically. A ground-glass joint was used for connecting the flask and column, the design and method of operation being that described by Smith and Adkins.² The temperature of the bath and column heater was so adjusted that the rate of distillation was 3–4 drops per minute, the spiral being well covered with returning liquid.

3. Suitable ranges for taking off fractions at various pressures on the first fractionation are as follows: 6 g., 152–157°/10 mm.; 176 g., 157–160°/10 mm.; 119 g., 160–180°/10 mm.; 126 g., 180–183°/10 mm.; 163 g., 115–123°/1 mm.; 115 g., 123–130°/1 mm.; 141 g., 130–133°/1 mm.; 29 g., below 91.5°/0.5 mm.; 116 g., 91.5–94.5°/0.5 mm.; 71 g., 94.5–115°/0.5 mm.; 170 g., 115–118°/0.5 mm.; 28 g., 118–125°/0.5 mm. Upon refractionation cuts were made as follows: 6 g., 152–157°/10 mm.; 161 g., 157–162°/10 mm.; 81 g., 162–171°/10 mm.; 64 g., 171–180°/10 mm.; 120 g., 180–183°/10 mm.; 198 g., 112–116°/1 mm.; 72 g., 116–129°/1 mm.; 147 g., 129–133°/1 mm.; 8 g., below 91.5°/0.5 mm.; 172 g., 91.5–94.5°/0.5 mm.; 10 g., 94.5–115.2°/0.5 mm.; 200 g., 115.2–118.2°/0.5 mm.; 25 g., 118.2–125°/0.5 mm. The temperature at which the esters distil varies with the rate of distillation and with the details of construction and operation of the column. The figures given above are intended to suggest the approximate ranges for cutting fractions.

4. This procedure has been used successfully for many years in the preparation of ethyl laurate,

caprylate, and myristate by the alcoholysis of cocoanut oil (1 kg.) in ethanol (1.9 kg.) with hydrogen chloride (50 g.) as a catalyst.³ The method differs slightly from the one described above. The alcoholysis is complete after 15 or 20 hours, and the solution is then neutralized to methyl orange with barium carbonate. The mixture is added to an equal volume of a saturated sodium chloride solution, whereupon 1100–1300 g. of the mixture of crude ethyl esters separates. This mixture of esters is washed with water and fractionated as described above. The yields are approximately 50 g. of ethyl caprylate, 350 g. of ethyl laurate, and 60 g. of ethyl myristate from 1 kg. of cocoanut oil.

5. The methyl myristate obtained (n_D^{25} 1.4353) showed a melting point of 19° when at equilibrium with the liquid. The methyl palmitate (n_D^{25} 1.4391 when supercooled) gave a melting point of 29.5°.

6. Myristic and palmitic acids can be obtained from their esters by the procedure in *Org. Syntheses Coll. Vol. 1*, 379 (1941). From 100 g. of methyl myristate is obtained 85–89 g. (90–95%) of colorless myristic acid melting at 52–53°. From 100 g. of methyl palmitate is obtained 84–88 g. (90–95%) of colorless palmitic acid melting at 62–63°.

3. Discussion

Of the early references to the preparation of methyl myristate and methyl palmitate, few are of preparative value. Methyl myristate can be prepared by the fractional distillation of the methyl esters from ucuhuba fat⁴ and from cocoanut oil.^{5,6} Methyl palmitate can be prepared in a similar manner from cocoanut oil⁶ and from bayberry wax.^{7,8}

Myristic and related acids may be prepared synthetically by a mixed Kolbe reaction.⁹

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 2*, 372

References and Notes

1. Simons and Wagner, *J. Chem. Education*, **9**, 122 (1932).
2. Smith and Adkins, *J. Am. Chem. Soc.*, **60**, 662 (1938).
3. *Organic Chemical Reagents*, Vol. 3, p. 62, University of Illinois, Urbana, Illinois, 1921.
4. Verkade and Coops, *Rec. trav. chim.*, **46**, 528 (1927).
5. Taylor and Clarke, *J. Am. Chem. Soc.*, **49**, 2829 (1927).
6. Lepkovsky, Feskov, and Evans, *J. Am. Chem. Soc.*, **58**, 978 (1936).
7. Wenzel, *Ind. Eng. Chem. Anal. Ed.*, **6**, 1 (1934).
8. McKay, *J. Org. Chem.*, **13**, 86 (1948).
9. Greaves, Linstead, Shephard, Thomas, and Weedon, *J. Chem. Soc.*, **1950**, 3326.

Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

bayberry wax

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

methanol (67-56-1)

sodium chloride (7647-14-5)

barium carbonate (513-77-9)

Myristic acid (544-63-8)

Methyl myristate (124-10-7)

palmitin (544-76-3)

palmitic acid (57-10-3)

ethyl laurate (106-33-2)

ethyl myristate (124-06-1)

Methyl palmitate (112-39-0)

myristin (629-59-4)

myristate

ethyl caprylate (106-32-1)

Caprylate

methyl orange (547-58-0)