Organic Syntheses

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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 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.

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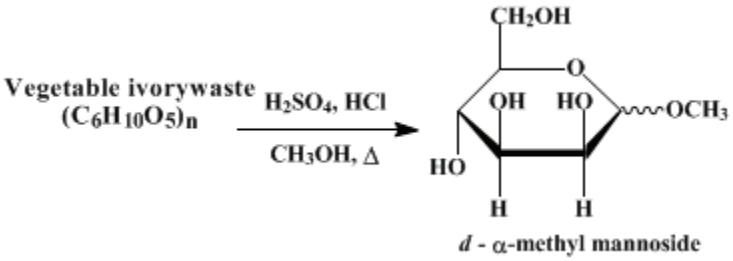
Organic Syntheses, Coll. Vol. 1, p.371 (1941); Vol. 7, p.64 (1927).

α-METHYL MANNOSIDE

[Mannoside, α-methyl-, *d*-]



d - α-methyl mannoside

Submitted by C. S. Hudson
Checked by Frank C. Whitmore and R. D. Greene.

1. Procedure

One kilogram of dry finely ground vegetable ivory waste (Note 1) is added gradually to 1250 g. of 85 per cent sulfuric acid in an 8-l. (2-gallon) enameled vessel (Note 2) at such a rate as to keep the temperature at 30–35° (one to two hours). The mass is well kneaded (Note 3) and then kept at about 25° for fifteen hours (Note 4). A mixture of 1 l. of acetone-free methyl alcohol and 250 cc. of pure concentrated hydrochloric acid (sp. gr. 1.19) (Note 5) is kneaded into the soft mass, which is then transferred to a 12-l. flask. The flask is adjusted on a large steam bath (Note 6); 6 l. of absolute methyl alcohol is added; and the mixture is refluxed eight hours.

At the end of this time the mixture is cooled somewhat, and 100 g. of decolorizing carbon and 150 g. of infusorial earth or fuller's earth are added, and refluxing is resumed for one-half hour. The solution is filtered hot with suction through a Büchner funnel previously heated by blowing steam into the side neck of the suction flask (Note 7). The cake is washed with 500 cc. of hot absolute methyl alcohol. The filtration is likely to be slow unless a large funnel (30 cm.) is used. The light yellow filtrate soon begins to deposit crystals (Note 8). It is kept in an ice box twenty to fifty hours. The crystals are filtered by suction, washed with 50 cc. of absolute methyl alcohol, then with 50 cc. of dry acetone, and dried on porous plates at room temperature. The yield is 480–520 g. The mannoside is pure enough for most chemical purposes. It melts at about 170° and has a rotation in water of + 78.6°. If a purer product is desired, the mannoside may be crystallized from four parts of 80 per cent ethyl alcohol with 80–90 per cent recovery if the mother liquors are worked up. Slight acidity in the solution used in recrystallization should be carefully neutralized with ammonia. The recrystallized mannoside melts at 188–189° and has a rotation of $[\alpha]_D^{20}$ + 80.8°.

2. Notes

1. The ivory nut waste was obtained from the Rochester Button Company, Rochester, N. Y. It was ground in a mill, dried to constant weight at 100°, and sifted through a 20-mesh screen (8 per cm.).
2. The bottom of an Elyria enameled kettle was used. A crock can be used almost as conveniently. On smaller runs a large porcelain mortar was used.
3. The kneading can conveniently be done by means of a heavy stick, the end of which has been thoroughly charred in a fire and then polished to remove loose carbon. Stirring is not practicable.
4. A convenient method of heating is to suspend a 60-watt electric light about 20 cm. above the mixture.
5. Later experiments indicate that the addition of hydrochloric acid is not essential since the sulfuric acid is sufficient to cause the formation of the mannoside (C. S. Hudson, private communication).
6. The flask may be immersed half way in a large kettle of water heated on a large radial burner.
7. Another convenient device for rapid filtration is to use a large Witt plate in a steam funnel attached to a suction flask.
8. In some runs spontaneous crystallization is slow to start. It is advantageous to inoculate the solution

with a crystal of the mannoside.

3. Discussion

α-Methyl mannoside can be prepared from mannose[1] or mannan triacetate[2] by the action of methyl alcohol and hydrochloric acid.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 541

References and Notes

1. Fischer and Beensch, Ber. **29**, 2928 (1896).
2. Patterson, J. Chem. Soc. **123**, 1139 (1923).

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

α-METHYL MANNOSIDE

mannan triacetate

Mannoside, α-methyl-, d-

ethyl alcohol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methyl alcohol (67-56-1)

acetone (67-64-1)

decolorizing carbon,
carbon (7782-42-5)

mannose