



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.

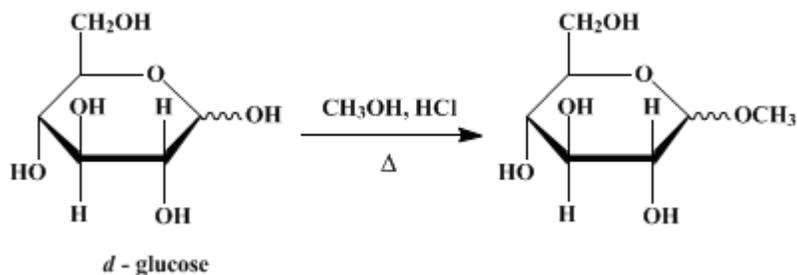
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.364 (1941); Vol. 6, p.64 (1926).

α -METHYL *d*-GLUCOSIDE

[Glucoside, α -methyl-, *d*-]



Submitted by B. Helferich and W. Schäfer.

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1. Procedure

Dry hydrogen chloride (p. 293), is passed into 200 g. (251 cc., 6.2 moles) of anhydrous methyl alcohol (Note 1), with ice cooling and exclusion of moisture, until the increase in weight amounts to 5 g. This solution is then diluted with 1800 g. of methyl alcohol, a 0.25 per cent solution of hydrogen chloride being thus obtained. To this is added 500 g. (2.77 moles) of finely powdered anhydrous *d*-glucose (Note 2), and the mixture boiled under reflux for seventy-two hours, a clear solution being obtained after the first fifteen minutes' boiling. It is well to attach a soda-lime tube to the upper end of the condenser, in order to exclude moisture. The clear pale yellow solution is cooled to 0°, and crystallization induced by scratching or by inoculation with a trace of α -methyl *d*-glucoside. After twelve hours at 0° the first crop is filtered by suction and washed twice with 100-cc. portions of cold methyl alcohol. The yield is 85–120 g. of a product melting at 165°.

The mother liquor and washings are returned to the flask and again boiled for seventy-two hours under reflux. The liquid is concentrated to 800 cc. and again chilled to 0°, inoculated, and allowed to stand at 0° for twenty-four hours. The second crop of glucoside so obtained is filtered by suction and washed with three 100-cc. portions of cold methyl alcohol. This yield is 110–145 g., melting at 164–165°. The mother liquor and washings are combined and concentrated to about 300 cc., chilled to 0°, and again inoculated and allowed to stand for twenty-four hours. The resulting mush of crystals is diluted with twice its weight of absolute methyl alcohol, and, after standing twenty-four hours at 0°, the third crop of glucoside is filtered (Note 3). This is recrystallized from 2.5 parts of methyl alcohol. The yield is 30–36 g., melting at 164–165°.

The total yield amounts to 260–266 g. (48.5–49.5 per cent of the theoretical amount). The product is contaminated by slight traces of *d*-glucose and possesses a very faint reducing power towards Fehling's solution. For complete purification it is recrystallized (with practically no loss and practically no change in melting point) from five parts of methyl alcohol with the use, if necessary, of decolorizing carbon.

2. Notes

1. All the methyl alcohol used in this preparation must be anhydrous and free of acetone.
2. Slight impurities in the *d*-glucose are apt strongly to color the reaction mixture but do not materially affect the yield.
3. The final mother liquor, on long standing, deposits a further crop (about 6 g.) of crystals which melt at 94–96° and consist largely of β -methyl glucoside. A further quantity of the α -glucoside may be obtained by distilling all the methyl alcohol and boiling the residue with methyl alcoholic hydrogen chloride; it is questionable, however, whether the yield repays the time spent on the operation.

3. Discussion

α -Methyl *d*-glucoside can be prepared by heating [glucose](#) with an alcoholic solution of [hydrochloric acid](#),¹ and biochemically from [glucose](#), [methyl alcohol](#) and water.² The procedure described is based on that of Fischer,¹ with simplifications due to Bourquelot;¹ and good yields have been reported with 3 per cent [hydrochloric acid](#) with a shorter period of refluxing.³

References and Notes

1. Fischer, Ber. **28**, 1151 (1895); Bourquelot, Ann. chim. (9) **3**, 298 (1915); Zemplen and Tulok; Abderhalden, "Biochemisches Handlexikon," **10**, 770 (1923) (unpublished observation); Patterson and Robertson, J. Chem. Soc. 300 (1929).
 2. Bourquelot, Hérissé and Bridel, Compt. rend. **156**, 491 (1913); Aubry, J. pharm. chim. (7) **10**, 202 (1914).
 3. Patterson and Robertson, J. Chem. Soc. 300 (1929).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

β -methyl glucoside

α -METHYL *d*-GLUCOSIDE

Glucoside, α -methyl-, *d*-

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

[methyl alcohol](#) (67-56-1)

[acetone](#) (67-64-1)

[decolorizing carbon](#) (7782-42-5)

[glucose](#),
[d-Glucose](#) (492-62-6)

[glucoside](#)

[\$\alpha\$ -glucoside](#) (492-62-6)