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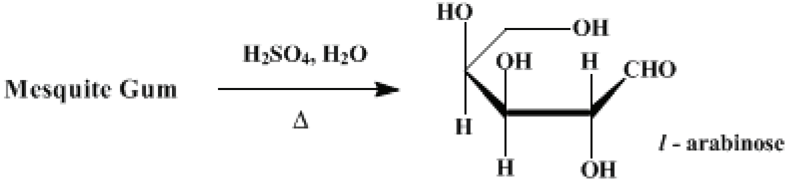
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.008.0018

Organic Syntheses, Coll. Vol. 1, p.67 (1941); Vol. 8, p.18 (1928).

l-ARABINOSE



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1. Procedure

Five hundred grams of mesquite gum (Note 1) is dissolved (Note 2) in 3 l. of cold water in a 5-l. round-bottomed flask; a cold solution of 125 g. of concentrated sulfuric acid in 80 cc. of water is added and the mixture warmed at 80° for six hours (Note 3) in a large water bath. The acid is neutralized by gradual addition of 140 g. of powdered calcium carbonate (Note 4), and the solution with excess calcium carbonate is heated in a boiling water bath for one hour to complete the neutralization. The calcium sulfate is filtered off and washed with about 2 l. of hot water. The filtrate is concentrated in an evaporating dish (Note 5) on the boiling water bath to a volume of 650–700 cc.

The solution is transferred to a 3-l. flask, using about 50 cc. of water for rinsing, and to it is added, with violent (Note 6) shaking, twice its volume (1400–1500 cc.) of 95 per cent ethyl alcohol. The solution is decanted from the gummy residue and the latter extracted three times with methyl alcohol under reflux, each time with 500 cc. of the solvent. In order to remove all the arabinose from the salts the precipitate is dissolved in 200–220 cc. of water, transferred to an evaporating dish, and 400 cc. of 95 per cent ethyl alcohol is stirred in with a heavy rod. The clear alcohol solution is decanted and the solid triturated twice with 300-cc. portions of methyl alcohol. All the alcoholic extracts (both ethyl and methyl) are combined, shaken thoroughly, and 95 per cent ethyl alcohol added as long as any appreciable precipitate forms (Note 7). The solution is allowed to stand for some hours until it is clear, decanted, and concentrated under reduced pressure on a boiling-water bath to a thin sirup (Note 8). Crystallization usually begins as soon as the sirup is cool, though it is sometimes necessary to seed with arabinose.

After crystallization has begun, 100 cc. of 95 per cent ethyl alcohol is stirred in, care being taken not to precipitate any appreciable amount of gum. Crystallization is allowed to become complete in a cool place, occasionally stirring with a heavy rod. After about two days the crystalline arabinose is filtered off and washed with 200 cc. of 95 per cent ethyl alcohol. To secure further crops of arabinose from the mother liquor and washings, the solvent is distilled off under reduced pressure on the boiling-water bath, and the residual gum dissolved in 200 cc. of hot methyl alcohol (Note 9). The solution is cooled, seeded with arabinose if necessary, set in the refrigerator for at least one day and the arabinose filtered off.

After the first two crops of crystals have been secured, the organic salts that originally dissolved along with the arabinose begin to interfere with the crystallization. To remove these, the solvent is distilled off under reduced pressure on the boiling-water bath, the residue dissolved in approximately 200 cc. of boiling methyl alcohol, and 95 per cent ethyl alcohol added slowly with shaking until no more precipitate forms (about 40 cc. is necessary). The solution is allowed to cool and is decanted from the gummy salts; the solvent is then distilled from the sugar on the steam bath, finally under reduced pressure. The sugar is dissolved in a minimum volume of hot methyl alcohol, cooled, seeded with arabinose if necessary, set in the refrigerator to crystallize and the arabinose filtered off. If an appreciable amount of mother liquor is obtained, a fourth crop of crystals can be secured without again removing the gummy salts. In this way a total yield of 180–230 g. of crude arabinose can be obtained from the gum. The first two crops of crystals are easily obtained and amount to approximately 90 per cent of the total yield. The melting point of the crude sugar varies from 147 to 152°.

The crude powdered sugar is purified by heating 200 g. of it for forty-five minutes on the boiling-water bath with 300 g. of glacial acetic acid,[1] allowing to cool, filtering off the arabinose, washing it with 500 cc. of 95 per cent ethyl alcohol in four portions, and drying at 50–60°. It then weighs about 182 g. and melts at 155–157°. It may be recrystallized from five times its weight of 76 per cent ethyl alcohol, with the use of 10 g. of decolorizing charcoal (Norite). The yield is about 127 g., and the melting point is 155–157°; the crystals are now perfectly colorless.

2. Notes

1. Mesquite gum is collected in the southwestern United States and northern Mexico. It is carried by most drug stores in this region and may be purchased from the Martin Drug Company of Tucson, Arizona.
2. If the mixture of mesquite gum and water is allowed to stand for ten hours with frequent shaking it will form a clear solution. If the mixture of gum and water is heated in the boiling water for one hour with frequent stirring the gum will also dissolve but the resulting solution is turbid.
3. Most of the arabinose is liberated during the first three hours' heating. The longer heating is necessary only in case the highest yield of arabinose is desired or the salts are to be used later for the preparation of galactose. No galactose is liberated by heating to 80° for six hours. However, some of this sugar is produced at 100° and seriously interferes with crystallization of the arabinose.
4. The solution is apt to foam over during neutralization. This may be prevented by adding to the foaming solution from time to time small amounts of *n*-butyl alcohol to break up the bubbles.
5. The solution may foam so badly that it is difficult to distil off the water under reduced pressure. In checking, it has been found possible to do so if as much as 200–300 cc. of butyl alcohol has been added during neutralization.
6. If the mixture is merely gently shaken at this point much arabinose is contained with the precipitate, and the yield falls to as low as 30 per cent of the amount obtained otherwise.
7. Appreciable amounts of organic salts dissolve during the extraction of the sugar and interfere seriously with the crystallization of the latter. Most of the salts are precipitated by addition of 95 per cent ethyl alcohol, leaving the sugar in solution.
8. If all the water is removed at this stage by heating the gum under reduced pressure for some time, the sugar will not crystallize readily.
9. Methyl alcohol, purified by distillation over quicklime, is the most satisfactory solvent for use in crystallizing the arabinose from the gummy mixture; ethyl alcohol at this stage usually causes the precipitation of a gum.

3. Discussion

Arabinose can be prepared by the hydrolysis of cherry gum,[2] beet pulp, cholla gum,[3] gum acacia[4] and mesquite gum.[5] The chief advantages of the preparation from mesquite gum are that the material is readily available in large amounts, the process is simple, and the yield relatively large. The present procedure is a modification of the original method of Anderson and Sands.[6]

References and Notes

1. Hudson and Dale, J. Am. Chem. Soc. **39**, 322 (1917).
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3. Gaertner, Z. Ver. deut. Zucker-Ind. 232 (1919) [C. A. **14**, 1455 (1920)]; Harding, Sugar, **24**, 656 (1922) [C. A. **17**, 1164 (1923)].
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5. Carrington, Haworth, and Hirst, J. Chem. Soc. **1934**, 1653.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethyl alcohol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

methyl alcohol (67-56-1)

calcium carbonate (471-34-1)

calcium sulfate (7778-18-9)

arabinose (28697-53-2)

sugar

galactose (492-62-6)

butyl alcohol,
n-butyl alcohol (71-36-3)

decolorizing charcoal (Norite) (7782-42-5)

l-ARABINOSE