

## Note

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### Procedure for reducing D-arabino-hexosulose to a mannitol-rich mixture of D-mannitol and D-glucitol

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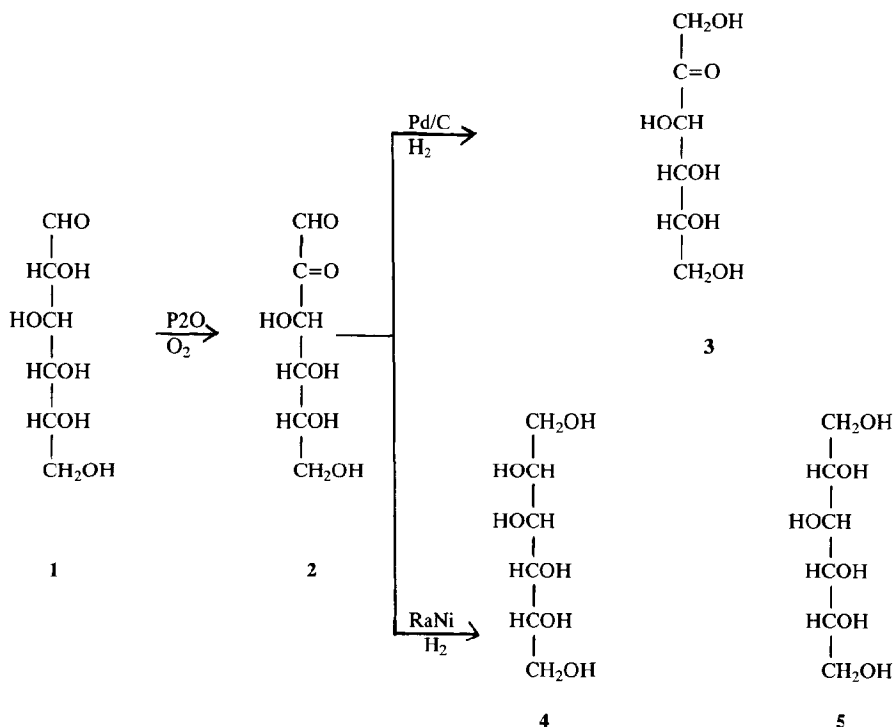
D-arabino-Hexosulose (D-glucosone, **2**) can now be conveniently produced by the enzymic reaction of pyranose-2-oxidase (P2O) with D-glucose<sup>1</sup> (**1**). D-arabino-Hexosulose has been efficiently and selectively reduced to D-fructose (**3**) by catalytic hydrogenation with palladium-on-carbon<sup>2</sup>. We now report a procedure for reducing **2** to a mannitol-rich mixture of D-mannitol (**4**) and D-glucitol (sorbitol, **5**). The method uses catalytic hydrogenation with Raney nickel, and yields **4** and **5** in 3:1 ratio. This ratio is unlike that obtained by catalytic hydrogenation of D-glucose (which yields exclusively D-glucitol) or by catalytic hydrogenation of D-fructose (which yields **4** and **5** in 1:1 ratio).

#### RESULTS AND DISCUSSION

D-Mannitol and D-glucitol are two commercially important alditols. Because D-mannitol commands a higher price than D-glucitol, producers of D-mannitol have sought to optimize its yield from glucose-based feedstocks. Reduction of corn syrup yields exclusively D-glucitol, whereas reduction of either high-fructose corn syrup or invert sugar yields D-mannitol and D-glucitol in only 1:2 ratio<sup>3,4</sup>.

Surprisingly, we found that D-arabino-hexosulose (**2**) is readily reduced to a mannitol-rich mixture of D-mannitol and D-glucitol by catalytic hydrogenation with Raney nickel. Neidleman *et al.*<sup>5</sup> previously attempted the reduction of **2** by hydrogen with Raney nickel, and reported the formation of a small proportion of D-fructose and some further-reduced products. However, the analytical method used did not permit further characterization of the mixture. Analysis of the mixture showed complete conversion of **2** into a product mixture containing D-mannitol and D-glucitol in the ratio of 3.2:1. Quantitation with sugar standards by l.c. accounted for 89 ± 10% of the total carbohydrate mass as these two products.

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There was the possibility that the reduction of **2** to a mannitol-rich mixture proceeded through D-fructose. This hypothesis was examined by catalytically hydrogenating a 3% aqueous solution (pH 4.5) of D-fructose under conditions identical to those described for the hydrogenation of **2**. Analysis of the mixture showed complete conversion of D-fructose and a product mixture containing mannitol and D-glucitol in the ratio of only 1.2:1. These results indicate that the reduction of D-glucosone to a mannitol-rich mixture cannot be explained solely on the basis of a D-fructose intermediate.

#### EXPERIMENTAL

*Reduction procedure.* — A 3% aqueous solution (pH 4.5) of D-arabino-hexosulose (**2**) was prepared from D-glucose<sup>1</sup>. To 4 mL of this solution, placed in a microhydrogenator apparatus (Supelco, Inc.), 250 mg of Raney nickel (Pfaltz and Bauer Co.) was added. The mixture was stirred under 51 kPa of hydrogen gas for 10 h at 25°.

*Analytical method.* — The mixture was analyzed by liquid chromatography (l.c.), with a Bio-Rad Aminex HPX-87C Carbohydrate column. The mobile phase was water at 85° and the solvent flow through the column was set at 0.6 mL/min. Detection was by refractive index. Known sugars and alditols had the following re-

tention times in this system: D-glucose (11.4 min.), D-*arabino*-hexosulose (12.3 min.), D-mannose (13.0 min.), D-fructose (14.2 min.), D-mannitol (18.3 min.), and D-glucitol (22.4 min.).

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