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Note

Convenient, laboratory procedure for reducing D-glucosone to D-fructose

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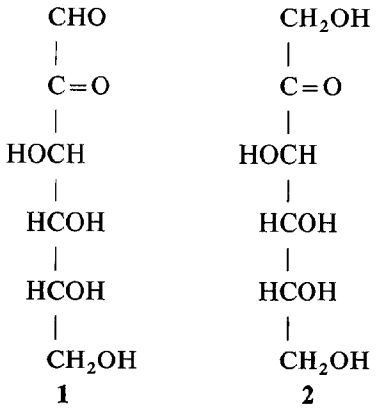
D-*arabino*-Hexos-2-ulose (D-glucosone, **1**) can now be conveniently produced by the enzymic reaction of pyranose-2-oxidase on D-glucose[1]. Previous attempts to reduce D-glucosone efficiently and selectively to D-fructose (**2**) had been only partially successful. Both zinc dust in aqueous acetic acid[2], and sodium borohydride[3], have been used, but these reduction methods were not selective, as D-fructose, D-glucose, and D-mannose, and alditols were formed.



We now report a convenient, laboratory procedure for reducing D-glucosone (**1**) to D-fructose (**2**). The method uses catalytic hydrogenation, and is >90% selective for the formation of D-fructose.

EXPERIMENTAL

Reduction procedure. — A solution of D-glucosone (1 g) in distilled water (20 mL) was placed in a micro-hydrogenator (Supelco, Inc.), and the catalyst, 5% palladium-on-carbon (500 mg; from Aldrich Chemical Co.), was slowly added. Hydrogen at a pressure of 50 lb.in.$^{-2}$ was introduced, and with vigorous stirring,

the reaction was conducted for 15 h at 25°. The mixture was filtered, first through Whatman No. 1 filter-paper, and then through a 0.22-μm filter. The filtrate was lyophilized, to yield solid D-fructose.

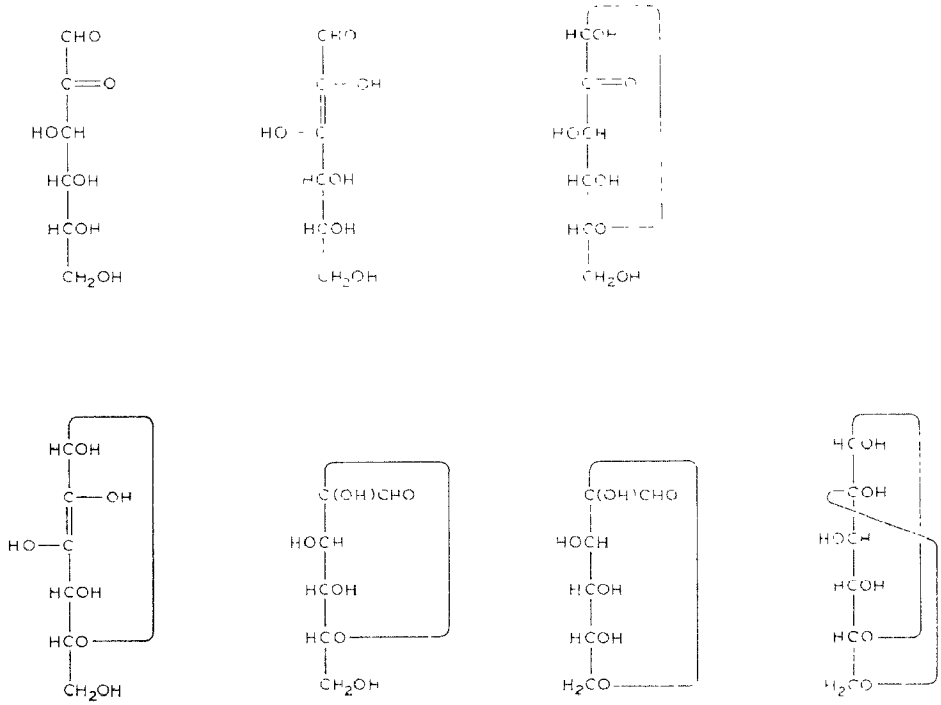
Analytical methods. — The reduction of D-glucosone was monitored by high performance liquid chromatography (h.p.l.c.) as previously described[1]. D-Fructose, D-glucosone, D-glucose, and other sugars are readily detected by this analytical method[4].

The reduction product from D-glucosone was co-chromatographed with authentic D-fructose in the following, thin-layer chromatography (t.l.c.) system: Avicel-coated glass-plates, developed with 4:4:1:2 (v/v) isopropyl alcohol–pyridine–acetic acid–water. The plates were then sprayed either with triphenyltetrazolium chloride reagent (1% TTC in 0.5M NaOH) or biphenyl–aniline phosphoric acid–ethyl acetate (0.15 g/0.8 mL/11 mL/100 mL) reagent.

A Perkin-Elmer Model 241 polarimeter was used to measure the specific rotation of aqueous solutions.

RESULTS AND DISCUSSION

The catalytic hydrogenation of D-glucosone faced two potential problems. One was control of the selectivity of the reduction. The structure of D-glucosone has been



Structures proposed for D-glucosone

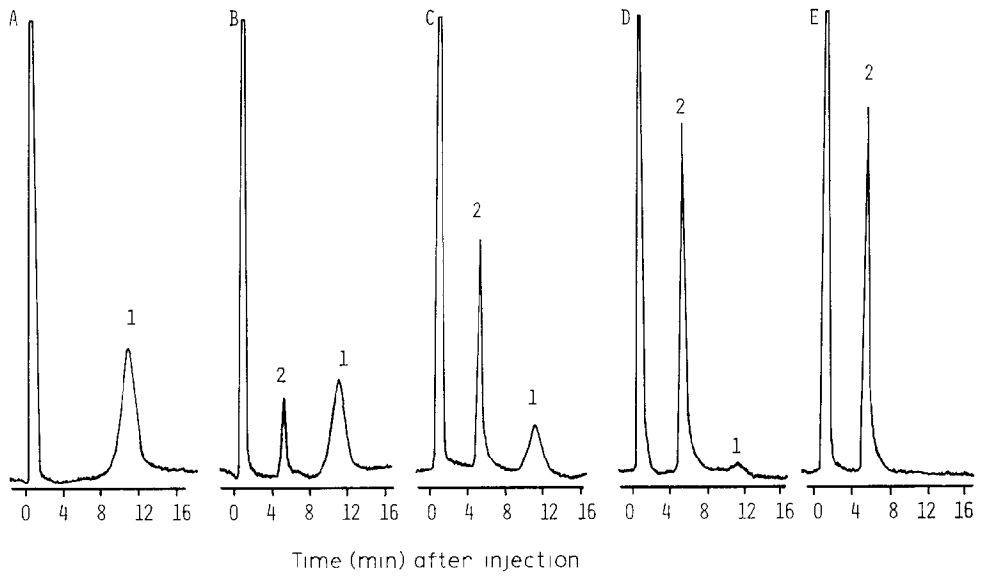


Fig. 1. H.p.l.c. monitoring of the catalytic hydrogenation of D-glucosone to D-fructose at reaction times of (A) 0, (B) 2, (C) 6, (D) 12, and (E) 15 h. [Assay conditions are described in the text. Peaks: 1, D-glucosone, and 2, D-fructose.]

a point of much discussion in past years[5,6], and some of the structures proposed for this compound are presented. Therefore, it was difficult to predict with certainty whether reduction of the aldehyde at C-1 (to yield D-fructose) or of the ketone at C-2 (to yield D-glucose) would be favored. The second problem was to be able to stop the reduction as soon as all of the D-fructose had been formed, as D-fructose is itself capable of being reduced.

Surprisingly, we found that the D-glucosone was readily reduced to D-fructose by catalytic hydrogenation. Fig. 1 shows the results obtained for the experimental conditions described. The reduction is highly selective, and other products were not detected. Other catalysts were tried, but 5% palladium-on-carbon yields the best results[7].

The reduction product of D-glucosone was co-chromatographed with authentic D-fructose and D-glucosone in t.l.c. D-Glucosone gave a streak, R_F 0.40–0.48, whereas D-fructose gave a spot at R_F 0.56. With the triphenyltetrazolium chloride spray-reagent, both D-glucosone and D-fructose gave a red spot instantly. With the biphenyl–aniline–phosphoric acid–ethyl acetate spray-reagent, D-glucosone gave a purple, and D-fructose, a yellow, spot, on heating for 10 min at 95°. The reduction product of D-glucosone and authentic D-fructose showed identical results in t.l.c. The reduction product of D-glucosone and authentic D-fructose showed almost identical specific rotations; $[\alpha]_D^{20}$ (degrees): D-glucosone (substrate), −9.8; reduction product of D-glucosone, −89.1; authentic D-fructose, −92.4.

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