THE PREPARATION OF L-SORBOSE FROM 5-*KETO*-D-GLUCONIC ACID (L-SORBURONIC ACID)[1]

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ABSTRACT

L-Sorbose has been prepared from 5-*keto*-D-gluconic acid.

INTRODUCTION

The most convenient method of preparation of L-sorbose is undoubtedly from the biochemical oxidation of sorbitol (1). The purpose of this communication is to demonstrate how D-glucose can be converted to L-sorbose by purely chemical transformations. The starting product was the calcium salt of 5-*keto*-D-gluconic acid (L-sorburonic acid) which had been prepared by biochemical oxidation of D-glucose (4). Salts of this acid can be prepared by prolonged oxidation of D-glucose with bromine (3) or electrolytically (2). When the calcium salt was shaken with methanolic hydrogen chloride it dissolved with the formation of a mixture of products composed mainly of the methyl glycoside methyl ester of 5-*keto*-D-gluconic acid. The carbomethoxy group of this glycoside was reduced with sodium borohydride to the alcohol with the formation of methyl L-sorbofuranoside from which L-sorbose was prepared by hydrolysis.

Since the oxidation of sugars by bromine water to 5-*keto*hexonic acids is a general reaction (3) the interconversion of aldoses to ketoses with concomitant inversion of the chain of hydroxyl groups becomes possible.

EXPERIMENTAL

Solutions were evaporated under reduced pressure. Optical rotations were measured in water at 20°±2° (unless otherwise stated). Sugars were separated chromatographically in either (*a*) ethyl acetate - acetic acid - formic acid - water (18:3:1:4, v/v) or (*b*) *n*-butanol–water–pyridine (18:3:3, v/v), and detected with the *p*-anisidine–hydrochloride spray.

Methyl 5-keto-D-Glucofuronic Acid Methyl Ester

The calcium salt of 5-*keto*-D-gluconic acid hydrate ($2\frac{1}{2}$, H_2O) (22 gm.) was suspended in methanol (500 ml.) and hydrochloric acid (d. 1.12, 20 ml.) added. The mixture was stirred overnight when a clear solution resulted. The pale yellow reaction mixture was heated at 40°C. for 24 hr., cooled, and then passed down columns of Amberlite resin 1R120 and 1R4B, which had been washed previously with dry methanol. The effluent was concentrated to a sirup (17 gm.) which was dissolved in acetone and filtered from insoluble material. The resultant methyl ester methyl glycoside was obtained as a pale yellow

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non-reducing sirup (14.2 gm.) $[\alpha]_D$ −24° (*c*, 3.6 in MeOH). Found: OMe, 28.1%. Calc. for $C_8H_{14}O_7$: OMe, 27.9%. The product contained three components, detected chromatographically, which moved, relative to rhamnose (R_{RH}), at the rates 1.25, 1.59, and 1.98 (solvent (*b*)). They gave yellow orange spots with the *p*-anisidine spray. The fastest moving material was present in traces only. 5-*keto*-D-Gluconic acid had R_{RH} 0.95 in solvent (*a*).

Methyl L-Sorbofuranoside and L-Sorbose

The methyl ester methyl glycoside (2 gm.) was dissolved in water (10 ml.) and sodium borohydride (0.5 gm.) added. The solution became warm and changed color from pale yellow to pale green. After 24 hr., excess of acetic acid was added and the solution was deionized on Amberlite resins 1R120 and 1R4B. On concentration a sirup (1.28 gm.) remained which contained five components. These materials moved on the chromatogram relative to rhamnose at the rates 0.38, 0.91, 1.07, 1.87, and 2.12 (solvent (*b*)). The slowest moving component which reduced Fehling's solution was identified as sorbose, and results probably from the hydrolytic action of the acidic resin on the methyl furanoside. The components with R_{RH} 0.91 and 1.07 behaved like methyl sorbofuranoside whilst the fastest two components which were present in trace amounts only were not identified. The mixture was heated with *N* sulphuric acid for three hours at 100°C., cooled, neutralized ($BaCO_3$), and filtered. The filtrate on concentration gave crystalline L-sorbose, which was recrystallized from methanol. The product (0.71 gm.) had m.p. 165°C. not depressed on admixture with an authentic specimen, moved on the chromatogram at the same rate as sorbose, and had $[\alpha]_D$ −41° (*c*, 1.1). Found: C, 40.1; H, 6.9%. Calc. for $C_6H_{12}O_6$: C, 40.0, H, 6.7%.

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