

1. Lindberg, B. and Lundström, H. *Acta Chem. Scand.* **20** (1966) 2423.
2. Kenne, L., Larm, O. and Svensson, S. *Acta Chem. Scand.* **26** (1972). *In press.*
3. Kenne, L., Larm, O. and Svensson, S. *To be published.*
4. Honeyman, J. *J. Chem. Soc.* **1946** 990.
5. Hough, L. and Jones, J. K. N. *J. Chem. Soc.* **1952** 4349.
6. Lawton, B. T., Szarek, W. A. and Jones, J. K. N. *Carbohyd. Res.* **10** (1969) 456.
7. Theander, O. *TAPPI* **48** (1965) 105.

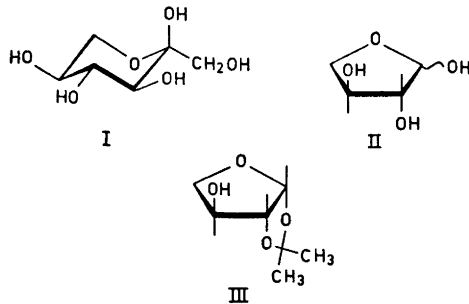
Received May 20, 1972.

## Oxidation of Carbohydrate Derivatives with Silver Carbonate on Celite. IV. Oxidation of L-Sorbose, an Alternative Synthesis of L-Threose

SVEIN MORGENTIE

*Department of Chemistry, Agricultural College, N-1432 Ås-NLH, Norway*

Three of the four aldotetroses are readily prepared from different aldohexoses and pentoses by common degradation reactions. An analogous synthesis of the fourth aldotetrose, L-threose, is forbidden by the lack of a readily available precursor with a correct configuration. The most convenient existing method for the preparation of L-threose seems to be periodate oxidation of 1,3-*O*-benzylidene-L-arabinitol,<sup>1</sup> which involves preparation of the starting material. It has been found in this laboratory that silver carbonate on Celite, reported in previous papers in this series to shorten the carbon chain of aldoses<sup>2</sup> and derivatives,<sup>3,4</sup> is a convenient degradation reagent also for ketoses. The present communication reports its application in preparation of L-threose from the commercially available, and inexpensive L-sorbose. A more detailed report on the oxidation of ketoses will be published elsewhere.



L-Sorbose (I) is completely oxidized in methanol at 40° within 40 min. The product exhibits strong infrared absorption at 1735  $\text{cm}^{-1}$  and the major component of the product mixture is detectable on a thin-layer plate by spray reagents for reducing sugars as well as for esters. This compound gives L-threose (II) on acid hydrolysis and subsequent treatment of the hydrolysate with anion exchanger. The initially formed product is in light of these facts assumed to be a glycolic ester of L-threose, resulting from glycol-cleavage between C-2 and C-3 of L-sorbose in a cyclic form.

The threose formed in this reaction is contaminated with small amounts of a compound which is assumed on chromatographic evidence to be glyceraldehyde. The tetrose is, however, pure enough to allow direct preparation of crystalline 1,2-*O*-isopropylidene- $\beta$ -L-threofuranose (III), by treatment with acetone-sulphuric acid. The yield of this compound was about 40% based on L-sorbose. If a chromatographically pure threose is desired, this is readily obtained by hydrolysis of the 1,2-*O*-isopropylidene derivative (III) with aqueous acetic acid.

*Experimental.* Thin-layer chromatography was performed on silica gel in the solvent systems (V/V): (A) benzene-ethanol 5:2 and (B) chloroform-methanol 30:1, paper chromatograms were run on Whatman No. 1 paper in (C) butanol-pyridine-water 5:3:2. As spray reagents were used diphenylamine-aniline-phosphoric acid<sup>5</sup> and hydroxylamine ferric chloride.<sup>6</sup>

*Oxidation of L-sorbose (I).* L-Sorbose (I) (1 g) in methanol (200 ml) was stirred at 40° for 40 min with silver carbonate on Celite<sup>7</sup> (22 g), solid material was filtered off and the solvent evaporated under reduced pressure. The resulting syrupy residue showed strong

infrared absorption at  $1735\text{ cm}^{-1}$ , thin-layer chromatography revealed the presence of a major component, detectable with both spray reagents, and at least two faster moving products in minor amounts. Hydrolysis of the syrup in 0.05 M sulphuric acid at  $60^\circ$  overnight and subsequent treatment of the solution with Dowex 1 ion exchange resin (regenerated with bicarbonate), afforded after evaporation of the solvent a colourless syrup (440 mg). Paper chromatography indicated the presence of only one component, indistinguishable from authentic D-threose, thin-layer chromatography in addition showed the presence of minor amounts of a compound indistinguishable from authentic D-glyceraldehyde.

*1,2-O-Isopropylidene-β-L-threofuranose (III)*. The crude L-threose (II) was shaken with acetone (40 ml) containing sulphuric acid (0.3 ml) for 3 h at room temperature. The solution was neutralized with solid sodium bicarbonate, after filtration the solvent was evaporated under reduced pressure, and the residue dissolved in benzene (50 ml). The benzene solution was extracted three times with water (20 ml portions); evaporation of the water under reduced pressure gave chromatographically homogeneous (solvent B) 1,2-O-isopropylidene-β-L-threofuranose (III) as a colourless syrup which solidified on standing. The yield was 345 mg (39 % based on L-sorbose). After recrystallization from ether-petroleum ether (b.p.  $40-65^\circ$ ) it had m.p.  $84-85^\circ$  (reported for the D-enantiomer<sup>8</sup>  $84^\circ$ ) and  $[\alpha]_D +13^\circ$  (c 1, acetone) (reported for the D-form<sup>8</sup>  $-15.3^\circ$ ).

*L-Threose (II)*. 1,2-O-Isopropylidene-β-L-threofuranose (III) (145 mg) was heated to  $100^\circ$  for 4 h in 30 % aqueous acetic acid. The solvents were evaporated under reduced pressure giving chromatographically homogeneous L-threose (II) as an almost colourless syrup. The yield was 105 mg (96 %), and  $[\alpha]_D +12^\circ$  (c 1, water) (lit.<sup>9</sup>  $+13.2^\circ$ ).

*Acknowledgement.* The author wishes to thank Miss Astrid Fosdahl for valuable technical assistance.

1. Gatzi, K. and Reichstein, T. *Helv. Chim. Acta* **21** (1938) 195.
2. Morgenlie, S. *Acta Chem. Scand.* **26** (1972) 1709.
3. Morgenlie, S. *Acta Chem. Scand.* **25** (1971) 2773.
4. Morgenlie, S. *Acta Chem. Scand.* To be published.
5. Schwimmer, S. and Bevenue, A. *Science* **123** (1956) 543.

6. Abdel-Akher, M. and Smith, F. J. *Am. Chem. Soc.* **73** (1951) 5859.
7. Balogh, V., Fetizon, M. and Golfier, M. *Angew. Chem.* **81** (1969) 423.
8. Steiger, M. and Reichstein, T. *Helv. Chim. Acta* **19** (1936) 1016.
9. Hockett, R. C., Deulofeu, V., Sedoff, A. L. and Mendive, J. R. *J. Am. Chem. Soc.* **60** (1938) 278.

Received May 16, 1972.

## On the Molecular Structure of Cyclopentadienylberyllium Borohydride, $C_5H_5BeBH_4$

D. A. DREW, GRETE GUNDERSEN and  
ARNE HAALAND

*Department of Chemistry, University of Oslo,  
Blindern, Oslo 3, Norway*

A series of cyclopentadienyl beryllium compounds,  $C_5H_5BeX$  where  $X = CH_3$ , Cl, Br,  $BH_4$ , has recently been synthesized by Drew and Morgan.<sup>1</sup> The compounds are monomeric in the gas phase and in benzene solution. Infrared absorption spectra show that the cyclopentadienyl rings have  $C_{5v}$  symmetry, *i.e.* that they are of the *penta-hapto* type. The room temperature PMR spectrum of  $(C_5H_5)BeBH_4$  in toluene shows that the four  $BH_4$  protons are equivalent on the NMR time scale, cooling to  $-80^\circ$  did not give separate signals for bridging and terminal hydrogen atoms.

Previously we have determined the molecular structures of  $C_5H_5BeCH_3$  and  $C_5H_5BeCl$  by gas phase electron diffraction;<sup>2</sup> we now report the result of an attempt to determine the molecular structure of  $C_5H_5BeBH_4$ .

Cyclopentadienylberyllium borohydride was supplied by Drew and Morgan. The electron scattering pattern was recorded on Balzers Eldiograph KD-G2. The sample reservoir was maintained at  $60^\circ$  and the