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Preliminary communication

Formation of L-*glycero*-tetrulose from D-*threo*-2,5-hexodiulosonate

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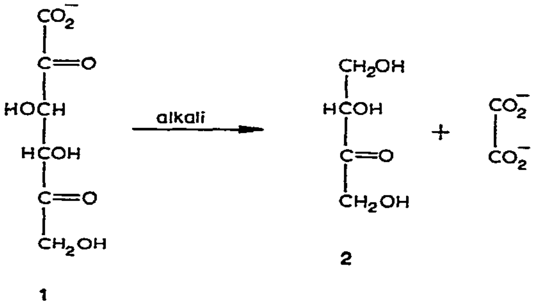
During an investigation of the stability of calcium D-*threo*-2,5-hexodiulosonate[1] (1) in aqueous solution, it was found that, in neutral or slightly acidic solution, 1 was degraded at C-2, with the elimination of oxalate, to L-*glycero*-tetrulose (2).

The degradation of 1 (10% aqueous solution), in the presence of the amount of calcium hydroxide required to combine with the oxalic acid formed and to maintain the pH at 7.0, gave an ~50% yield of 2, after 20 days at 30°.

The apparent course of the reaction is as follows:

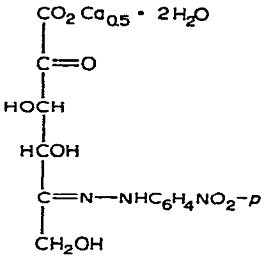


The crude product 2 could be isolated from the reaction mixture by removing the precipitate of calcium oxalate, concentrating the filtrate to dryness, extracting with hot ethanol, and evaporating the extract to a brown syrup. After passing an aqueous solution of this syrup through a column of an ion-exchange resin, column chromatography on silica gel (5:4:1 acetone–methanol–water) was used for purification of 2.

The identification of the product, a faintly yellow syrup, as L-*glycero*-tetrulose was mainly based on the characterization of its phenylosazone[2] and the following analytical data: $[\alpha]_D^{20}$ +12° (*c* 6, water)[3]; $\nu_{max}^{liq.}$ 3400–3300 cm^{-1} (OH); n.m.r. (D_2O): δ 3.85 (d, 2 H, *J* 4 Hz, -C-CH_2OH), 4.42 (t, 1 H, *J* 4 Hz, O=C-C*H*OH-), and 4.54 (s, 2 H, O=C-CH_2OH).

The starting material (1) used in this experiment was prepared by the action of an *Acetobacter* sp. on D-glucose[4]. The structure of 1 was shown by its elemental analysis and the spectral data of its mono-*p*-nitrophenylhydrazone (3): λ_{max}^{EtOH} 394 nm (log ε 3.46;

ν_{max}^{KBr} 3400, 1720, 1590, 1380, and 830 cm^{-1}; n.m.r. (Me_2SO-d_6 + D_2O): δ 4.47 (s, 2 H, -CH_2OH), 4.50 (d, 1 H, J 2 Hz, -COCHOH-), 4.82 (d, 1 H, J 2 Hz, -CHOH-C=NNH-), 7.17 (d, 2 H, J 9.5 Hz, H-2 and H-6 of phenyl), and 8.02 (d, 2 H, J 9.5 Hz, H-3 and H-5 of phenyl). The p-$NO_2C_6H_4$NNH- group was deduced to be at C-5 of **1**, from the reaction products of **1** with arylhydrazines[5].



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