

Short Communications

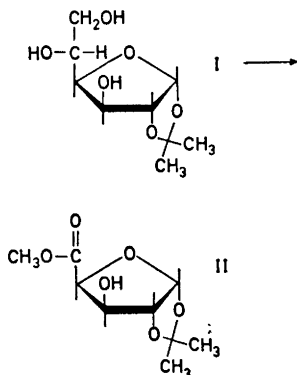
Oxidation of Carbohydrate Derivatives with Silver Carbonate on Celite. IX. Oxidation of 1,2-*O*-Isopropylidene- α -D-glucofuranose

SVEIN MORGENLIE

Agricultural University, Department of Chemistry, N-1432 Ås-NLH, Norway

In previous papers in this series, oxidation of ketoses,^{1,2} aldoses,^{3,4} and derivatives of aldoses⁵⁻⁷ with silver carbonate on Celite has been described. At temperatures below 60°C, the oxidant seems to have negligible effect on nonreducing carbohydrate derivatives. In boiling methanol, however, some 1,2-*O*-isopropylidene derivatives of aldohexofuranoses have been found to undergo a slow oxidation, involving the exocyclic glycol group. The present paper reports the oxidation of 1,2-*O*-isopropylidene- α -D-glucofuranose (I) to methyl 1,2-*O*-isopropylidene- α -D-xylofuranuronate (II).

After 10 h in boiling methanol, 1,2-*O*-isopropylidene- α -D-glucofuranose (I) is completely oxidized by silver carbonate on Celite, and the xyluronic acid derivative



(II) is the only product, obtained in about 70 % yield. Small amounts of an other compound are chromatographically detectable during the course of the reaction. This compound undergoes, however, a relatively rapid further oxidation, and it is presumably an intermediate in the oxidation of 1,2-*O*-isopropylidene- α -D-glucofuranose (I) to the xyluronic acid derivative (II).

The physical data of the product are in good agreement with those previously reported for methyl 1,2-*O*-isopropylidene- α -D-xylofuranuronate.⁸ The identity is further established by borohydride reduction and subsequent acid hydrolysis to xylose, and by spectroscopy. The proton magnetic resonance spectrum shows coupling constants $J_{1,2} = 3.5$ Hz, $J_{2,3} < 0.5$ Hz, and $J_{3,4} = 3.0$ Hz, in good agreement with those reported for other 1,2-*O*-isopropylidene-furanoses with *xylo*-configuration. The small coupling constant between the *trans* oriented protons at C-2 and C-3 is generally observed in spectra of this type of compounds.⁹

A more detailed investigation of this reaction and its applicability to analogous compounds is in progress.

Experimental. Paper chromatography was run on Whatman No. 1 paper in the solvent system (v/v) butanol-pyridine-water 5:3:2, thin layer chromatography on silica gel G plates in benzene-ethanol 4:1, and electrophoresis on Whatman No. 1 paper in borate buffer, pH 10. The proton magnetic resonance spectrum was recorded on a Varian HA-100 spectrometer.

*Oxidation of 1,2-*O*-isopropylidene- α -D-glucofuranose (I).* 1,2-*O*-Isopropylidene- α -D-glucofuranose (I) (500 mg) was stirred in boiling methanol (250 ml) with silver carbonate on Celite¹⁰ (12 g) for 5 h. More oxidant (5-6 g) was then added, and the oxidation continued until thin layer chromatography showed complete oxidation of the starting material (3-4 h). A single spot was observed on the thin layer plate, detectable with diphenyl-

amine-aniline-phosphoric acid¹¹ as well as with hydroxylamine-ferric chloride.¹² The solution was filtered, the solvent evaporated and the residue extracted with chloroform. Evaporation of the chloroform gave crystalline methyl 1,2-*O*-isopropylidene- α -D-xylofuranuronate (II) (337 mg, 68 %). After sublimation *in vacuo*, it had m.p. 104–106°C (lit.⁸ 103–104°C), and $[\alpha]_D -30^\circ$ (*c* 2, methanol) (lit.⁸ -32.8°). Strong infrared absorption was observed at 1745 cm⁻¹ (KBr), NMR signals were located at δ 1.30, 1.46, 3.74 (3 protons, singlets), 2.42 (1 proton, broad), 4.39, 4.48, 4.68, 5.95 (1 proton, doublets).

The product (20 mg) in water (3 ml) was treated with sodium borohydride (100 mg) over night. The solution was then treated with Dowex 50 W ion exchanger (H⁺), filtered and the solvent evaporated. Boric acid was removed by repeated distillations of methanol from the residue, which subsequently was hydrolyzed in 30 % acetic acid for 4 h at 100°C. Removal of the water and acetic acid under reduced pressure gave a syrup which appeared homogeneous by paper chromatography and electrophoresis, indistinguishable from authentic xylose.

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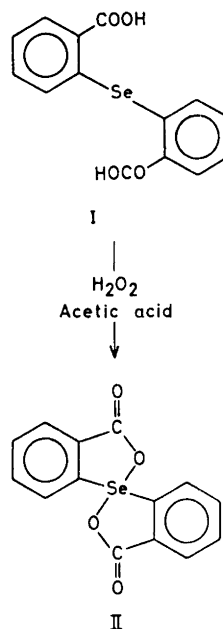
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Formation and Crystal Structure of 3,3'-Spirobi(3-selenaphthalide)

BIRGITTA DAHLÉN^a and
BJÖRN LINDGREN^b

^aCrystallography Group, Swedish Medical Research Council Unit for Molecular Structure Analysis, University of Göteborg, Fack, S-400 33 Göteborg 33, Sweden, and
^bInstitute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

The 3,3'-spiropi(3-selenaphthalide) (II) was first synthesized by Lesser and Weiss¹ by warming 2,2'-dicarboxy-diphenyl selenide (I) with concentrated sulphuric acid. This synthesis has now been re-investigated. Compound II has also been obtained when oxidizing I with hydrogen peroxide in acetic acid (Scheme 1). Infrared spectra and elemental analysis data of II are in good agreement with the proposed spiro-dilactone structure.



Scheme 1.

The analogous spiro-thia-dilactone has recently been synthesized and its crystal structure determined.^{2,3}