

Oxidation of Carbohydrate Derivatives with Silver Carbonate on Celite. III. Formation of Tetroses from D-Xylose and L-Arabinose

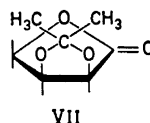
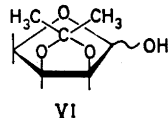
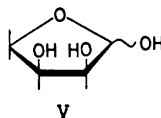
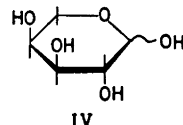
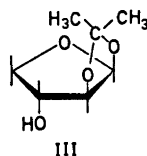
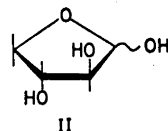
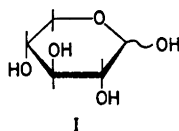
SVEIN MORGENLIE

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

The degradation of 3-*O*-methyl-D-glucose to 2-*O*-methyl-D-arabinose by silver carbonate on Celite was reported in a previous paper in this series.¹ Further degradation of the pentose derivative formed was prevented by the 2-*O*-substituent. It was of interest to investigate the effect of the oxidant also on unsubstituted sugars, and the present communication reports the formation of tetroses as major products after oxidation of D-xylose and L-arabinose.

D-Xylose (I) was completely oxidized within 90 min at room temperature in methanol. The initially formed product was assumed on spectroscopic evidence to contain as major component a formyl ester, from which D-threose (II) was liberated by weak alkaline hydrolysis. The reaction mixture also contained an acidic product, and in addition a compound, chromatographically indistinguishable from glyceraldehyde, was observed after hydrolysis. The formyl derivative obviously results from a diol cleavage between C-1 and C-2 in a cyclic form of the pentose. This is in accordance with the observations made on oxidation of 3-*O*-methyl-D-glucose.¹ The possibility that two different formyl derivatives were present may not be excluded. When the reaction time was reduced to 80 min, the formation of detectable amounts of glyceraldehyde was prevented, and D-threose (II) was obtained in a purity sufficiently high to allow direct preparation of its crystalline 1,2-*O*-isopropylidene derivative (III). The over all yield of this compound from xylose was about 40 %.

L-Arabinose (IV) was oxidized with a considerably lower speed, a reaction time of 6 h was necessary to bring about complete oxidation at room temperature. Oxidation at 40° for 20 min afforded after hydrolysis L-erythrose (V), contaminated with minor amounts of glyceraldehyde and



some unchanged pentose. An acidic component, removable with basic ion exchange resin, was also in this case observed in the product mixture. Acetonation of the crude tetrose gave the low melting 2,3-*O*-isopropylidene-L-erythrose (VI) in about 40 % over all yield, characterized by oxidation with silver carbonate on Celite in benzene² to the easily crystallizing 2,3-*O*-isopropylidene-L-erythrone-1,4-lactone (VII).

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,³ aniline oxalate and hydroxylamine—ferric chloride.⁴

Oxidation of D-xylose (I). D-Xylose (I) (0.5 g) in methanol (100 ml) was stirred at room temperature with silver carbonate on Celite⁵ (12 g) for 80 min. After filtration, a small portion of the solution was evaporated to a

syrup, which showed infrared absorption at 1725 cm^{-1} , characteristic of formyl esters.⁶ A shoulder at 1770 cm^{-1} was also observed. The methanolic solution was concentrated to a small volume (2–3 ml) and chloroform (50 ml) was added. After treatment of the solution with a little charcoal, it was filtered and then extracted three times with water (30 ml portions). To the combined water extracts was added sodium carbonate (0.5 g), and after 1 h the solution was treated with Dowex 50 W (H^+) and subsequently with Dowex 1 (HCO_3^-) ion exchange resins. Evaporation of the solvent gave a colourless syrup (225 mg), thin-layer and paper chromatography showed the presence of a compound indistinguishable from an authentic sample of L-threose, besides some unchanged D-xylose.

1,2-O-Isopropylidene- β -D-threofuranose (III). The crude D-threose (II) was shaken with acetone (40 ml) containing sulphuric acid (0.35 ml) for 3 h. The solution was neutralized with solid sodium bicarbonate, filtered and the solvent evaporated. The residue was dissolved in benzene (100 ml), and the benzene solution extracted three times with water (50 ml portions). Evaporation of the water under reduced pressure gave 1,2-O-isopropylidene- β -D-threofuranose (III) as a chromatographically homogeneous syrup (solvent B), which crystallized in the freezer. The yield was 205 mg, 38 % based on D-xylose. After recrystallization from diethyl ether–petroleum ether (b.p. $40-65^\circ$), it had m.p. $81-83^\circ$ (lit.⁷ 84°) and $[\alpha]_D -13^\circ$ (c 2, acetone) {lit.⁷ -15.3° }.

Oxidation of L-arabinose (IV). L-Arabinose (IV) (500 mg) in methanol (100 ml) was stirred with silver carbonate on Celite (12 g) for 20 min at 40° , work up as described above afforded a colourless syrup (200 mg), paper and thin-layer chromatography (solvents C and A, respectively) showed in addition to some unchanged pentose and minor amounts of glyceraldehyde, a major component indistinguishable from authentic D-erythrose.

2,3-O-Isopropylidene-L-erythrose (VI). The crude L-erythrose (V) was treated with acetone–sulphuric acid as described for D-threose (II). TLC (solvent B) showed the presence of a major component, indistinguishable from an authentic sample of 2,3-O-isopropylidene-D-erythrose, and minor amounts

of a faster moving component, presumably di-O-isopropylidene-L-arabinose, in the benzene solution of the reaction mixture. Extraction of the benzene solution with water as above, gave chromatographically homogeneous 2,3-O-isopropylidene-L-erythrose (VI) as a syrup, which solidified slowly in the freezer, and melted at room temperature. (Reported⁸ m.p. $29-31^\circ$ [$\alpha]_D +75^\circ$ (c 1, methanol){lit.⁸ $+72^\circ$ }. The yield was 218 mg, 41 % based on L-arabinose.

2,3-O-Isopropylidene-L-erythrono-1,4-lactone (VII). 2,3-O-Isopropylidene-L-erythrose (VI) (70 mg) in benzene (50 ml) was refluxed for 2 h with silver carbonate on Celite (2 g). The solution was filtered and the solvent evaporated under reduced pressure, the resulting syrup showed a single spot when subjected to TLC (solvent B), visualized with the hydroxylamine–ferric chloride reagent only. Crystallization from petroleum ether (b.p. $40-65^\circ$) gave 45 mg (65 %) of 2,3-O-isopropylidene-L-erythrono-1,4-lactone (VII) as needle-shaped crystals, m.p. $66.5-68^\circ$ (reported for the D-enantiomer⁹ $65-67.5^\circ$), $[\alpha]_D +105^\circ$ (c 1, water) (reported for the D-form⁹ -116°). Infrared absorption was observed at 1780 cm^{-1} (chloroform), characteristic of γ -lactones.

1. Morgenlie, S. *Acta Chem. Scand.* **25** (1971) 2773.
2. Morgenlie, S. *Acta Chem. Scand.* **25** (1971) 1154.
3. Schwimmer, S. and Bevenue, A. *Science* **123** (1956) 543.
4. Abdel-Akher, M. and Smith, F. *J. Am. Chem. Soc.* **73** (1951) 5859.
5. Balogh, V., Fetizon, M. and Golfier, M. *Angew. Chem.* **81** (1969) 423.
6. Thompson, H. W. and Torkington, P. *J. Chem. Soc.* **1945** 640.
7. Steiger, M. and Reichstein, T. *Helv. Chim. Acta* **19** (1936) 1016.
8. Baxter, J. N. and Perlin, A. S. *Can. J. Chem.* **38** (1960) 2217.
9. Schaffer, R. *J. Res. Natl. Bur. Std.* **A 65** (1961) 507.

Received March 21, 1972.