

A Simplified Synthesis of Penta-*O*-acetyl- α -*D*-altropyranose

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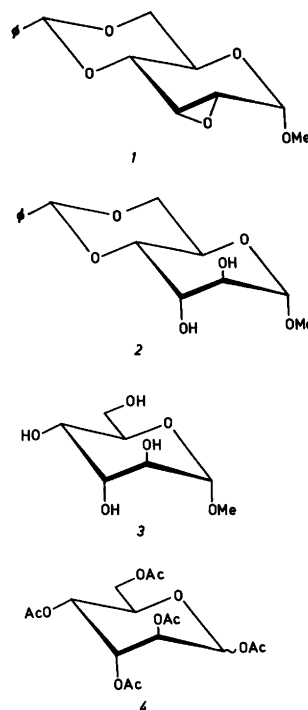
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The synthesis of penta-*O*-acetyl- α -*D*-altropyranose (α -4) is well-described,¹ and involves the reaction of the epoxide (1) with aqueous base to give 2 which on hydrolysis provides methyl- α -*D*-altropyranoside (3). Acetylation of the latter subsequently yields α -4, obtained in a total yield of 51% based on 1.¹ We have now found that 1 can be converted into a mixture of α -4 and β -4 in one step through treatment with a mixture of acetic anhydride and sulfuric acid. After crystallization of α -4 (54%) the material in the mother liquor consisted of a mixture of α -4 and β -4 in a ratio of 3:7 as seen from a ¹H NMR spectrum. When this mixture was subjected to the same conditions as described above an additional crop (27%) of α -4 could be isolated. After recrystallization of the combined products a total yield of 64% of α -4 was obtained.

Deacetylation of α -4 with methoxide¹ yielded *D*-altrose, characterized through its ¹³C NMR spectrum. It is important to avoid prolonged treatment with acidic ion exchange resin in the neutralization of the base because the acidic conditions, even at room temperature, can cause the formation of substantial amounts of 1,6-anhydro- β -*D*-altropyranose.

Experimental. Melting points are uncorrected. Optical rotations were measured on a Perkin Elmer 141 polarimeter. ¹H NMR and ¹³C NMR spectra were obtained at 270 MHz and 67.89 MHz, respectively, on a Bruker HX-270 NMR-instrument.

To a cooled suspension of 1 (20.0 g) in acetic anhydride (100 ml) a solution of concentrated sulfuric acid (2 ml) in acetic anhydride (100 ml) was added during 1 h. The reaction mixture was allowed to stand overnight at room temperature before it was poured into ice-water (2000 ml) and stirred for 2 h. Extraction with dichloromethane (3 × 100 ml) followed by washing with water, drying (MgSO₄), filtration and evaporation gave a syrup which could be crystallized from ethanol yielding (α -4) (16.0 g, 54%) m.p. 101–109 °C. Treatment of the mother liquor material with acetic anhydride as described above furnished an additional amount of α -4 (8.1 g, 27%). Recrystallization of the combined products from ethanol gave α -4 (19.0 g, 64%) m.p. 115–



117 °C, $[\alpha]_D^{20} = +61^\circ$ (*c* 1.2, CHCl₃); reported,¹ m.p. 118–119 °C, $[\alpha]_D^{20} = +63^\circ$ (CHCl₃).

Deacetylation of α -4 (5.0 g)¹ gave *D*-altrose as a syrup (2.25 g, 97%) characterized through its ¹³C NMR spectrum in D₂O (internal standard, dioxane = 67.40 ppm): α -Pyranose: 94.7 ppm (C-1, ¹J(C-H1) = 168 Hz); 71.2 (C-2); 71.1 (C-3); 66.0 (C-4); 72.0 (C-5); 61.6 (C-6). β -Pyranose: 92.6 ppm (C-1, ¹J(C-H1) = 162 Hz); 71.6 (C-2); 71.3 (C-3); 65.2 (C-4); 75.0 (C-5); 62.5 (C-6). α -Furanose: 102.2 ppm (C-1, ¹J(C-H1) = 173 Hz); 82.4 (C-2); 76.9 (C-3); 84.3 (C-4); 72.5 (C-5); 63.3 (C-6). β -Furanose: 96.2 ppm (C-1, ¹J(C-H1) = 175 Hz); 77.5 (C-2); 76.0 (C-3); 82.1 (C-4); 73.4 (C-5); 63.3 (C-6). The ratio between the anomers, determined from the ¹³C NMR spectrum, was α -F: β -F: α -P: β -P = 19:13:27:41, agreeing well with results published by Angyal and Pickles² on the basis of ¹H NMR data.

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1. Richtmeyer, N. K. *Methods in Carbohydrate Chemistry*, Academic, New York 1962, Vol. 1, p. 107.
2. Angyal, S. J. and Pickles, V. A. *Aust. J. Chem.* 25 (1972) 1692.

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