Note

Benzyl 2-deoxy-a-D-arabino-hexopyranoside

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The synthesis of benzyl 2-deoxy- α -D-*arabino*-hexopyranoside (1) was undertaken as the first step in a synthesis of 2-deoxy-D-*erythro*-hexos-3-ulose. An attempt to prepare 1 by the Fischer procedure, previously utilized for the preparation of benzyl glycosides¹⁻³, failed. However, when 2-deoxy-D-*arabino*-hexose was refluxed for 40 min in a mixture of benzyl alcohol, benzene and a strongly acidic, cation-exchange resin, with azeotropic removal of water, the benzyl glycoside was isolable crystalline in 60% yield.

Gas-chromatographic analysis of the product as its trimethylsilyl ether⁴ showed the presence of two components in a ratio of 9:1. This proportion was not appreciably changed after several recrystallizations. Hydrogenation of the product over 5% palladium on charcoal gave 2-deoxy-D-arabino-hexose as the only product, as shown by g.l.c. and mass spectrometry. The mass spectrum of the trimethylsilyl ether of the glycoside is consistent with a pyranoid structure. It showed no molecular-ion peak, but exhibited an M-91 peak diagnostic of the loss of a benzyl radical, and an M-103peak, rationalized as resulting from cleavage of the Me₃SiOCH₂ group from a pyranoid ring⁵. No peak at M-205, diagnostic of a furanoid structure was observed. The major component present was shown to be the α -anomer 1, on the basis of the 250-MHz n.m.r. spectrum. The anomeric proton resonated, as a quartet, at 4.90 p.p.m. having $J_{1,2a}$ 3.1 Hz and $J_{1,2e}$ 1.0 Hz. The observed coupling-constants are consistent with the α -configuration in the CI(D) conformation. The signal for H-1 of the β -glycoside could be detected at 4.99 p.p.m., but it was partially masked by the H-1 signal of the α -glycoside.

We have since applied this glycosidation technique to D-fructose, D-glucose, D-mannose, D-xylose, D-arabinose, and 2-deoxy-D-erythro-pentose. No crystalline product could be isolated from D-fructose or 2-deoxy-D-erythro-pentose, but the other four sugars gave benzyl glycosides in yields ranging from 55-70%. Details of these preparations and anomeric composition of the products will follow later.

The short reaction-time and simplicity of this procedure commend it for the small-scale synthesis of benzyl glycosides. In addition, yields generally equal or exceed those in the Fischer synthesis.

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EXPERIMENTAL

General methods. — G.I.c. was performed by using a Perkin-Elmer Model No. 900 gas chromatograph equipped with a flame-ionization detector; helium was the carrier gas. A $6 \text{ ft} \times 0.125$ in. OV-101 column was temperature-programmed at 5°/min from 115 to 250°. Coupled g.I.c.-mass spectrometry was performed on an LKB 9000 mass spectrometer with the same column, under identical conditions. Mass spectra were obtained at an ionizing potential of 70 eV. N.m.r. spectra were obtained with a 250-MHz n.m.r. spectrometer designed and built by the Carnegie-Mellon University chemistry department. The elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

Benzyl 2-deoxy- α -D-arabino-hexopyranoside (1). — To a mixture of 10 ml of benzene, 15 ml of benzyl alcohol and 250 mg of Dowex 50W-X8 in a 50-ml flask, equipped with a Barrett trap filled with benzene, and a reflux condenser, was added 1 g of 2-deoxy-D-arabino-hexose. The mixture was refluxed for 40 min. The flask was cooled in an ice bath and the resulting yellow suspension was filtered to remove the resin, which was washed with 5 ml of water. To the filtrate was added 75 ml of ether, and the mixture was extracted with two 35-ml portions of water. Hexane (25 ml) was added to the organic phase, which was extracted with an additional 35 ml of water. The combined water extracts were evaporated under diminished pressure to yield a colorless syrup that crystallized. Recrystallization of the solid from 1:1 ethyl acetatediethyl ether gave 0.92 mg (60%) of benzyl 2-deoxy- α -D-arabino-hexopyranoside (1), m.p. 131–133°, $[\alpha]_D^{25}$ +73° (c 1.7, water); λ_{max}^{KBr} 2.91 (OH), 13.6, 14.8 μ m (phenyl); n.m.r. data [(CD₃)₂SO-D₂O, 9:1]: δ 1.6 (m, $J_{1,2a}$ 3.1, $J_{2a,2e}$ 11.0, $J_{2a,3}$ 9.1 Hz, H-2a), 2.0 (m, $J_{1,2e}$ 1.0, $J_{2e,3}$ 4.5 Hz, H-2e), 4.4 and 4.6 (d, J 12 Hz, benzyl-methylene), 4.90 (q, H-1), 7.33 (s, phenyl).

Anal. Calc. for C₁₃H₁₈O₅: C, 61.41; H, 7.14. Found: C, 61.56; H, 7.25.

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