3-*O*-α-D-Glucopyranosyl-D-mannose

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In a recent synthesis of 3-*O*-β-D-glucopyranosyl-D-mannose carried out at this laboratory,[1] 3,4,6-tri-*O*-acetyl-1,2-*O*-methylorthoacetyl-α-D-glucopyranose [2] was condensed with benzyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside in the presence of mercuric bromide in nitromethane under the glycosylation conditions described by Kochetkov and co-workers.[2] The expected β-linked disaccharide derivative was obtained, but also, depending on the reaction conditions, appreciable amounts of the substituted α-linked title compound. The latter, 3-*O*-α-D-glucopyranosyl-D-mannose, is of immunochemical interest due to the occurrence of 3-*O*-α-D-glucopyranosyl-α-D-mannopyranose residues in the *Salmonella* serogroup C_1 hexasaccharide repeating unit.[3] The disaccharide, which has not been unambiguously synthesized before, has been described as one of the products of transglucosidation of phenyl α-D-glucopyranoside with mannose in the presence of brewer's yeast.[4] The present communication describes its isolation from the above reaction mixture.[1] The physical properties (m.p. 136–139°, $[\alpha]_D$ +96° of the previously described disaccharide [4] agree reasonably well with those of the synthetic product (m.p. 138–140°, $[\alpha]_D$ 87°). The structural assignment of the synthetic disaccharide described here is based on the optical rotation and elemental analysis of the product, hydrolysis and sugar analysis and also MS on the derived per-methylated 3-*O*-α-D-glucopyranosyl-D-mannitol.

Experimental. General methods were the same as those described in a previous paper.[1] 3,4,6-Tri-*O*-acetyl-1,2-*O*-methylorthoacetyl-α-D-glucopyranose [2] (3.44 g) and benzyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside [1] (4.25 g) were condensed in nitromethane (40 ml) containing mercuric bromide (128 mg) as previously described.[1] The product was deacetylated and the disaccharide derivative mixture freed from monomers by solvent partition. Reacetylation yielded a mixture containing benzyl 3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside as the major product which was purified by chromatography to yield 3.0 g pure material.[1] The remaining material (561 mg) was further separated by chromatography on silica gel (solvent, ethyl ether–hexane 2:1) to yield the presumed benzyl 3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (180 mg) in a chromatographically pure state. Deacetylation overnight at room temperature in methanol containing 1.67 % ammonia followed by catalytic hydrogenation in ethanol with 10 % palladium on charcoal afforded crystalline 3-*O*-α-D-glucopyranosyl-D-mannose, m.p. 138–140°, $[\alpha]_D$ +87° (*c*, 0.2, in water, final rotation, no mutarotation observed). (Found: C 42.1; H 6.62. $C_{12}H_{22}O_{11}$ requires: C 42.1; H 6.48.) Hydrolysis and sugar analysis [5] showed the presence of glucose and mannose in a ratio of 1:1. Reduction to the corresponding glucosylalditol and per-methylation [6] afforded a substance which, apart from minor difference in intensities, gave the same mass spectrum as that from per-methylated 3-*O*-β-D-glucopyranosyl-D-mannitol.[1,7]

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