Carbohydrate Research, 58 (1977) 217–218

Note

Synthesis of 4-*O*-α-L-rhamnopyranosyl-D-glucose

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(Received November 5th, 1976; accepted for publication, December 15th, 1976)

4-*O*-α-L-Rhamnopyranosyl-D-glucose, for which no synthesis has been reported hitherto, was first isolated[1] from *Acacia senegal* gum (gum arabic). The disaccharide was synthesised (10% overall yield) by condensation of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide with 1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose in benzene in the presence of mercury(II) acetate, followed by Zemplén deacetylation of the product. The synthetic disaccharide and that isolated by Aspinall showed identical behaviour in p.c. and t.l.c., and in g.l.c of their trimethylsilyl ethers.

Acid hydrolysis of the disaccharide gave L-rhamnose and D-glucose only (p.c.), and Kuhn methylation followed by acid hydrolysis gave 2,3,6-tri-*O*-methyl-D-glucose and 2,3,4-tri-*O*-methyl-L-rhamnose identified[2] by p.c. The configuration of the glycosidic linkage in the synthetic disaccharide was indicated by the optical rotation, which agreed with that of the authentic specimen.

EXPERIMENTAL

Melting points were determined by the Kofler method and are uncorrected G.l.c. was performed on a Varian Model 2740 dual-column gas chromatograph with hydrogen flame detectors, a differential electrometer, and a linear temperature programmer.

4-O-α-L-Rhamnopyranosyl-D-glucose. — A mixture of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (2.59 g, 7.4 mmol), mercury(II) acetate (1 g), and 1,2,3,6-tetra-*O*-acetyl-β-D-glucose[3] (2.53 g, 7.4 mmol) was shaken in dry benzene (40 ml) for 4 days protected from atmospheric moisture in the dark at room temperature. The mixture was then washed with water (4×), dried ($CaCl_2$), filtered, and concentrated. The colourless, syrupy residue (0.97 g) was treated with methanol (10 ml) and 0.1M methanolic sodium methoxide (1.2 ml) for 6 h at room temperature. The solution was concentrated at 40° under reduced pressure, and a solution of the residue in water was deionized with Dowex 50W-X2(H^+) resin, concentrated *in vacuo*, and then chromatographed on Whatman 3MM paper with 1-butanol-acetic acid-water (4:1:5, upper layer). The band having R_{GLC} 0.70 (test strips detected with aniline phosphate) was excised, and extracted with water. Concentration of the extracts *in* *vacuo* gave the title compound (240 mg), $[\alpha]_D$ −6° (*c* 1, water), which was treated with phenylhydrazine hydrochloride (200 mg) and sodium acetate (300 mg) in water (2 ml) at 100° for 2.5 h to give a phenylosazone, m.p. 165–167° alone or in admixture with the authentic compound (Found: C, 57.18; H, 6.33; N, 11.13. $C_{24}H_{32}N_4O_8$ calc.: C, 57.12; H, 6.39; N, 11.10%).

A solution of the disaccharide (50 mg) in 10% acetic acid (30 ml) was boiled under reflux for 3.5 h and then concentrated to dryness *in vacuo*, and excess of acetic acid was removed from the residue by co-distillation with water. P.c. of the residue with the above solvent system, and also with 1-butanol–ethanol–water (4:1:5, upper layer) and ethyl acetate–acetic acid–formic acid–water (18:3:1:4), revealed only rhamnose and glucose.

The synthetic and natural disaccharides showed identical behaviour in p.c. with these solvent systems and in t.l.c. on silica gel (Merck) with propan-2-ol–isopropyl ether–65% formic acid (4:3:3) and 1-butanol–acetic acid–ethyl ether–water (9:6:3:1). G.l.c. of the trimethylsilyl ethers[4] on a column (2 m × 2.2 mm) of 2.5% of SE-30 on Chromosorb W (80–100 mesh), with a nitrogen flow-rate of 50 ml/min and a temperature programme of 2°/min from 135°→240°, gave two peaks having retention times of 18.5 and 19.5 min.

ACKNOWLEDGMENTS

The author thanks Professor G. O. Aspinall (York University, Ontario) for a sample of 4-*O*-α-L-rhamnopyranosyl-D-glucose from *Acacia senegal* gum, and Professor M. Piattelli for his interest.

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