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KOENIGS-KNORR SYNTHESIS OF PART OF THE IMMUNODETERMINANT GROUP IN A STREPTOCOCCAL POLYSACCHARIDE:
2-O-α-L-RHAMNOPYRANOSYL-L-RHAMNOPYRANOSE

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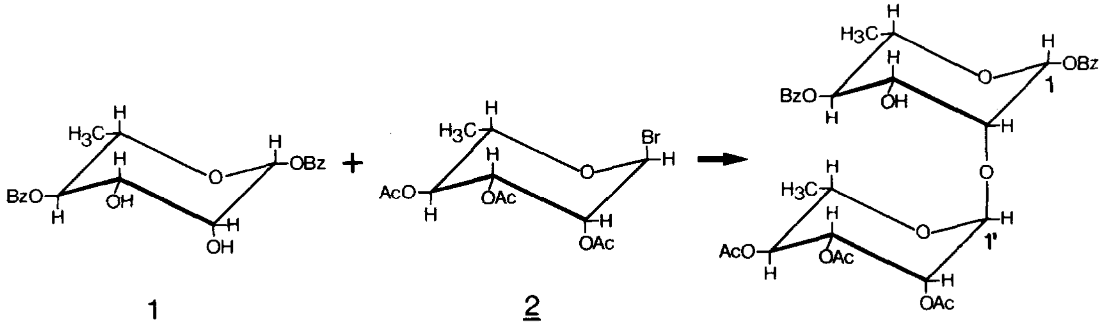
L-Rhamnose is the major constituent in streptococcal group specific carbohydrates[1]; one of these is the A-variant carbohydrate, a linear homopolymer of 1→2- and 1→3-linked L-rhamnose entities[2]. In order to study the chemistry and immunochemistry of this polysaccharide, 2-O-α-L-rhamnopyranosyl-L-rhamnopyranose was synthesized.



1 2 3

Benzylation[3] of 2,3-O-isopropylidene-L-rhamnose[4] and subsequent acid hydrolysis yielded 1, m.p. 75-76°C, $[\alpha]_D^{20}$ +46.8° (c 1.1, acetone) (lit.[3] m.p. 76-78°C, $[\alpha]_D^{20}$ +47°, acetone). ^{1}H nmr ($CDCl_3$, 270 MHz), δ:4.45 (d,1H, H-1), 3.94 (t, 1H, H-2), 3.60 (m, 1H, H-3), 3.35 (m, 1H, H-4), 3.29 (m, 1H, H-5), 1.37 (d, 3H, H-6). 2 (readily obtained from L-rhamnose[5], m.p. 65°C, $[\alpha]_D^{25}$ -161° (c 1.0 acetone) (lit.[5] m.p. 68°C; $[\alpha]_D^{18}$-160°)) has been reacted with 1 under the conditions of the Koenigs-Knorr reaction[6]. After purifying an aliquot of the reaction mixture by preparative TLC we obtained crystals of 3, Rf = 0.75, ethyl ether. By seeding the reaction mixture with these crystals 3 could be crystallized directly in a 30% yield. m.p. 161°C, $[\alpha]_D^{25}$ -24.55° (c 1, acetone), elemental analysis: C 62.05%, H 6.51% (theoretically C 62.33%, H 6.54%). The glycosidic linkage of 3 was determined to be 1→2 by p.m.r. spectroscopy.

After hydrogenolytic cleavage of the benzyl groups[7] and subsequent solvolysis of the resulting acetate[8], we obtained the free dissacharide, $[\alpha]_D^{25}$ -28.7°, elemental analysis: C 46.52%, H 7.21% (theoretically: C 46.45%, H 7.15%). ^{1}H nmr (D_2O, 270 MHz), δ:5.24 (s, 0.9H, H-1), 5.04(d, J:2Hz, 0.1H), 4.98 (d, $J_{1',2'}$:1.7Hz, 0.9H, H-1'), 4.90 (s, 0.1H). The predominating species was identified as 2-O-α-L-rhamnopyranosyl-L-rhamnopyranose according to chemical shift and coupling constant of the anomeric proton (H-1') in the nonreducing moiety[9,10].

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