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Note

Isolation of 6-(D-*glycero*-2,3-dihydroxypropyl)-2-(D-*threo*-trihydroxypropyl)pyrazine.

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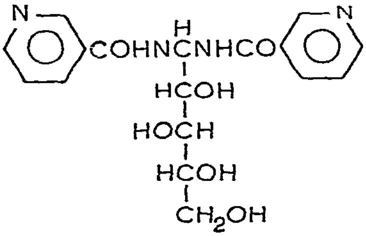
The reaction of ammonia with different monosaccharide pernicotinates was described in a previous paper[1]. In the case of D-mannose[1] and D-glucose[2] pentanicotinates, besides the corresponding 1-deoxy-1,1-bis(nicotinamido)alditols and *N*-nicotinoylglycosylamines, a pyrazine compound was also isolated, which was rather unusual in this type of reaction.

When the reaction was conducted with tetra-*O*-nicotinoyl-D-xylose, 1-deoxy-1,1-bis(nicotinamido)-D-xylitol (**1**) was obtained[1] in 13.2% yield, and we now report the isolation of the title compound (**2**); it crystallized in 2.7% yield after the residual syrup from the isolation of (**1**) had been exhaustively dried and treated with absolute ethanol.

The structure of compound **2** as 6-(D-*glycero*-2,3-dihydroxypropyl)-2-(D-*threo*-trihydroxypropyl)pyrazine was established by considering the configuration of the original free sugar and the structural determinations now described. It crystallized from isopropyl alcohol as needles of m.p. 120–121°, $[\alpha]_D^{20}$ −128° (*c* 1, water). Paper chromatography in 5:2:2 butyl alcohol–ethanol–water gave only one nonreducing spot (R_{Xyl} 1.2), revealed with ammoniacal silver nitrate[3]. U.v. (H_2O) λ_{max} 274 nm;



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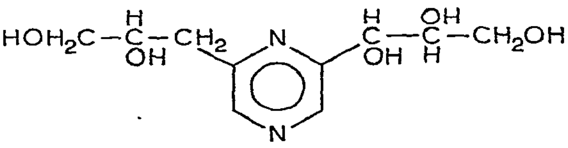

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n.m.r. data: aromatic protons of pyrazine ring at τ 1.33 (s) and 1.46 (s), H-1 at 4.97 (d), H-2 and H-2′ at 5.88 (m), C-3 and C-3′ methylene groups at 6.30 (m), and C-1′ methylene at 6.95.

Anal. Calc. for $C_{10}H_{16}N_2O_5$: C, 49.17; H, 6.60; N, 11.47. Found: C, 49.20; H, 6.58; N, 11.64.

Oxidation with periodate gave an initial uptake of 3 moles of periodate per mole and production of 2 moles of formaldehyde and 1 mole of formic acid. Afterwards, overoxidation[2] occurred, with an uptake of 1 mole more of periodate and release of 1 mole of formic acid. These results agree with those expected for structure **2**.

The pattern of substitution in the ring was ascertained by oxidation of **2** (10 mg) with 6% hydrogen peroxide (1 ml) and sodium hydroxide (30 mg). After heating for 45 min at 80°, a quantity (0.75 ml) of 100% hydrogen peroxide was added, and the solution was heated for 1 h more. After being acidified, the solution was chromatographed on paper by the ascending technique for 15 h by using 4:1:1 (v/v) butyl alcohol–formic acid–water[4]. Only one (red-violet) spot, R_F 0.67, was revealed with ferrous ammonium sulfate[5], coincident with the spot given by a pure specimen of 2,6-pyrazinedicarboxylic acid. Pure 2,5-pyrazinedicarboxylic acid gave a blue spot, R_F 0.49.

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