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SYNTHESIS OF 2-AMINO-2-DEOXY-α-D-GLUCOPYRANOSYL β-D-FRUCTOFURANOSIDE (2-AMINO-2-DEOXY-SUCROSE)

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2-Amino-2-deoxy-α-D-glucopyranosyl β-D-fructofuranoside (2-amino-2-deoxy-sucrose) was synthesized by condensation of 3,4,6-tri-O-acetyl-2-(2,4-dinitroanilino)-2-deoxy-α-D-glucopyranosyl bromide and 1,3,4,6-tetra-O-benzyl-D-fructofuranose with the aid of silver perchlorate and tribenzylamine in benzene, followed by removal of protecting groups.

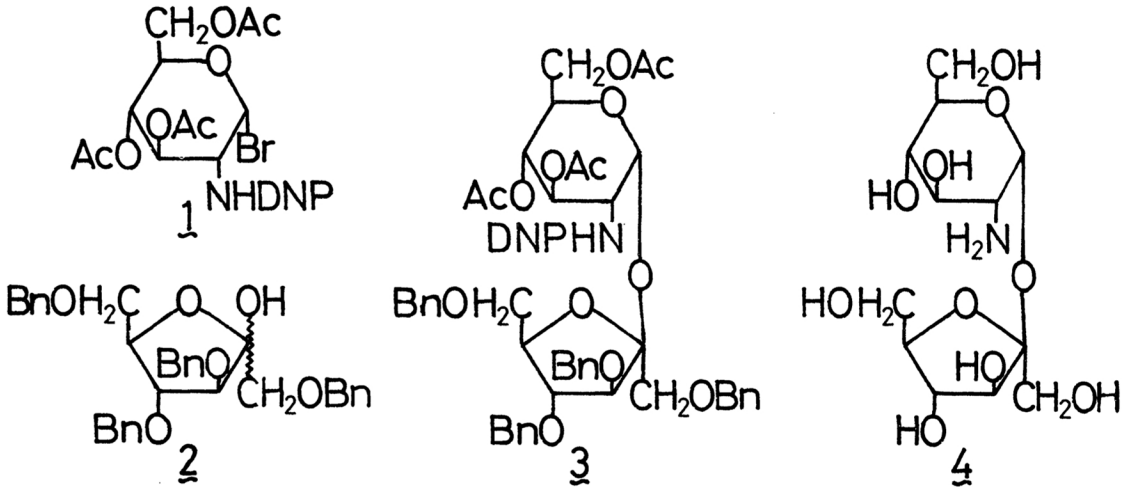
There have been several trials to synthesize aminodeoxysucroses but only compounds in which primary hydroxyl groups are replaced by an amino group have been synthesized.[1] We now wish to communicate the first synthesis of a derivative of sucrose having a secondary amino group; i.e., 2-amino-2-deoxy-α-D-glucopyranosyl β-D-fructofuranoside (4) (2-amino-2-deoxy-sucrose) has been synthesized by way of the condensation of 3,4,6-tri-O-acetyl-2-(2,4-dinitroanilino)-2-deoxy-α-D-glucopyranosyl bromide[2] (1) with 1,3,4,6-tetra-O-benzyl-D-fructofuranose[3] (2), using our modified Koenigs-Knorr reaction.[4]

An equimolar mixture of 1 (1.9 mmol), 2, silver perchlorate, and tribenzylamine in benzene (10 ml) was stirred for 24 h at room temperature in the dark. The resulting mixture was filtered and then chromatographed on silica gel using a solvent system of benzene and butanone to give 3,4,6-tri-O-acetyl-2-(2,4-dinitroanilino)-2-deoxy-α-D-glucopyranosyl 1',3',4',6'-tetra-O-benzyl-β-D-fructofuranoside (3), Rf = 0.40 (benzene : butanone = 20 : 1), $[\alpha]_D^{20}$ +36° (c 0.7, $CHCl_3$) (Found: C, 63.21; H, 5.92; N, 3.93%. Calcd for $C_{52}H_{55}N_3O_{17}$: C, 62.83; H, 5.58; N, 4.23%) in 22% yield and other condensation products (Rf = 0.38 and 0.32).

Compound 3 was successively subjected to de-O-acetylation with dil sodium methoxide, de-N-dinitrophenylation with Dowex 1x2 (OH) in aq acetone,[5] hydrogenolysis over palladium in aq acetic acid and then chromatography on Dowex 1x2 (OH) developed with water to afford sweet base, 4, $[\alpha]_D^{20}$ +72° (c 0.3, H_2O) (Found: C, 40.70; H, 7.18; N, 3.87%. Calcd for $C_{12}H_{23}NO_{10}\cdot 0.75H_2O$: C, 40.62; H, 6.95; N, 3.95%) in 12% yield from 1.

C-13 NMR of 4 in D_2O (Fig. 1) unequivocally shows that 4 is the 2-amino-2-deoxy- analog of sucrose.

Further characterization of 4 and identification of the minor condensation products are in progress.



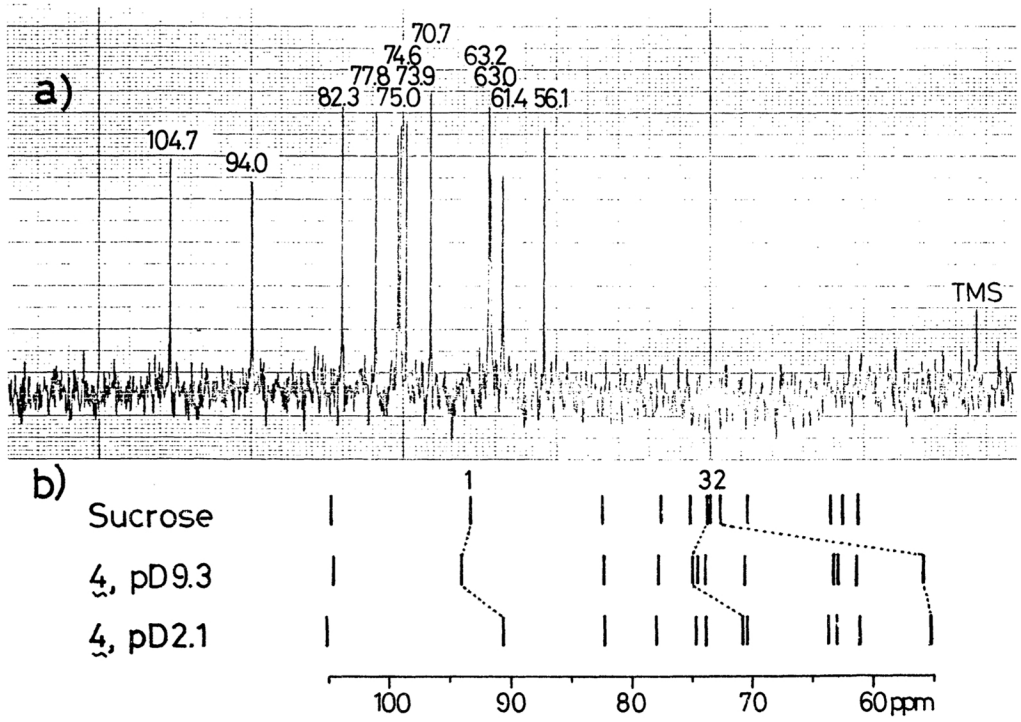


Fig. 1. a) FT C-13 NMR (25.1 MHz) of 4 in D_2O (pD = 9.3), b) Correlation diagram

References and footnote

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5) Yield of this step was 72%.

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