

# Reaction of Monosaccharides with Substituted Anilines and Phenylhydrazines: Schiff Bases vs. Glycosylamines as Crystalline Products

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Upon reaction with a nitrogenous base, a monosaccharide can yield an acyclic (Schiff base) derivative or a cyclic (glycosylamine) derivative as the crystalline product. We are conducting a crystallographic study of nitrogenous derivatives produced by the reaction of substituted anilines and phenylhydrazines with non-acetylated monosaccharides to determine what factors may favor formation of one form of the derivative over the other. Relevant structures published in the Cambridge Structural Database to date include derivatives of only D-ribose, D- and L-arabinose, D-xylose, D-glucose, D-mannose, and D-galactose, and for some of these monosaccharides only a few derivatives have been reported. Here we describe the molecular and crystal structures of N-(phenyl)-D-ribosepyranosylamine hemihydrate (I), 1-[2-(4-cyanophenyl)hydrazino]-1-deoxy- $\beta$ -D-glucopyranose (II), N-(2-fluorophenyl)- $\beta$ -D-galactopyranosylamine (III), N-(4-fluorophenyl)- $\beta$ -D-galactopyranosylamine (IV), N-(3-nitrophenyl)- $\beta$ -D-mannopyranosylamine (V), D-mannose 2-(2-fluorophenyl)hydrazone (VI), D-mannose 2-(4-fluorophenyl)hydrazone (VII), D-mannose 2-pyridinylhydrazone (VIII), and 1-[2-(pentafluorophenyl)hydrazino]-1-deoxy- $\beta$ -D-mannopyranose dihydrate (IX). The D-ribose aniline derivative (I) is cyclic, as are its two published aniline-based analogues but unlike its published phenylhydrazine-based analogue. The two monosaccharide molecules in the asymmetric unit of (I) assume 4C1 and 1C4 conformations, confirming spectroscopic results obtained by previous investigators. The D-glucose phenylhydrazine derivative (II) and the D-galactose aniline derivatives (III) and (IV) are cyclic in the solid state, as are all of the previously reported aniline- and phenylhydrazine-based derivatives of these two monosaccharides. Crystallization of D-mannose aniline derivative (V) as the glycosylamine and of D-mannose phenylhydrazine derivatives (VI), (VII), and (VIII) as Schiff bases is consistent with the apparent preferences shown by D-mannose based on previously published structures, but the D-mannose pentafluorophenylhydrazine derivative (IX) breaks with this trend, crystallizing as the glycosylamine.