Abstract

2-Amino-2-deoxysaccharides are present in many important classes of glycoconjugates and naturally occuring oligosaccharides, in which they are connected to other residues through either 1,2-*cis* or, more frequently, 1,2-*trans* glycosidic linkage. They are fundamental to biological processes such as cell-cell or cell-virus recognition, which makes them an attractive target in the study of immune system defects. With the growing demand for these biologically important derivatives, efforts to develop chemical methods for the synthesis of 2-amino oligosaccharides have also increased.

This work is focused on preparation of saccharide units, derived from D-glucosamine, D-galactosamine and D-mannosamine, and their application in the synthesis of branched oligosaccharides. Monosaccharide building blocks were designed in consideration of desired *O*-glycosidic bond configuration of oligosaccharides. Synthesis of glycosyl acceptors, suited for the synthesis of bi-antennary trisaccharides, was based on *trans*-diaxial oxirane ring opening of 1,6:2,3-dianhydrosugars by azide ion. Glycosyl acceptors for tetrasaccharide synthesis were prepared from commercially avaialable D-glucosamine and D-galactosamine. The anomeric hydroxyl group was protected as *n*-pentenyl glycoside, which can be later used as a precursor of spacer arm. Transformation of double bond into another functionality was verified by ozonolysis of two *n*-pentenyl glycosides.

The glycosylation method used in the oligosaccharide synthesis was chosen according to desired configuration of glycosidic bond. Trisaccharide consisting of 1,2-*cis* connected D-*gluco* and D-*galacto* units was prepared by trichloroacetimidate method, with glycosyl donor having a non-participating azido group in position C-2. On the other hand, participating effect of phthalimido group on C-2 of ethylthioglycosides enabled stereoselective formation of 1,2-*trans*-glycosides.

Besides the synthesis of 2-azido derivatives, both 1,6;2,3- and 1,6;3,4-dianhydrosaccharides were also used in the study of epoxide migration and *pseudo*-migration of α-hydroxy epoxides. Moreover, various halogen derivatives of 1,6-β-D-hexopyranoses were prepared. NMR was used for following the reaction mechanism and analysis of reaction mixtures. Experimental data were compared with theoretical calculations.