α-Selective Glycosidation of the Rare Sugar d-Tagatofuranose and the Synthesis of α-d-Tagatofuranosylceramide

Yui Makura,Akihiro Iyoshi,Makito Horiuchi,Yiming Hu,Masakazu Tanaka,Atsushi Ueda

Abstract

d-Tagatose is a rare sugar that exhibits intriguing biological properties, such as its role as a low-calorie sweetener and its ability to reduce the glycemic response. Consequently, the synthesis of d-tagatose derivatives is a crucial endeavor for the advancement of their functionalities, as well as elucidation of their biological properties. In this study, we present the α-selective glycosidation of a 1,3,4,6-tetra-*O*-benzoylated d-tagatofuranosyl donor with various glycosyl acceptors. In contrast to d-allulose, which is the C3,C4-epimer of d-tagatose and does not exhibit the neighboring group effect, the current d-tagatofuranosyl donor demonstrated significant neighboring group participation, achieving high α-selectivity ratios up to $\alpha:\beta = 99:1$. This method was also applicable to the synthesis of α-d-tagatofuranosylceramide, which has potential as a novel functional molecule. Meanwhile, the glycosylation of sterically congested glycosyl acceptors, such as 2-hydroxycumene, resulted in poor α-selectivity, which may be attributed to the interaction with the C1-benzoyloxy group of d-tagatofuranosyl donors in the transition state.