Full Stereocontrol in α-Glycosidation of 3-Deoxy-2-ketoaldonic Acids Using Macrobicyclic Glycosyl Donors; Sialic Acid and Kdo

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Sialic acid and Kdo (3-deoxy-d-manno-2-octulosonic acid) belong to the class of 3-deoxy-2-ketoaldonic acid and share common structural features, which make the stereoselective glycosidation of sialic acid and Kdo difficult.1,2 The oxocarbenium ion intermediates of the both are unstable owing to the anomeric carboxyl group and vulnerable to decomposition via 1,2-elimination, which is enhanced by the 3-deoxy structure. The absence of a hydroxyl group at the position adjacent to the anomeric center prevents neighboring participation in the stereocontrol. Recently, we reported that macrobicyclic sialyl donors, which were tethered at the anomeric carboxyl group and the C5 amino group, enabled the fully α-selective sialylation that were not affected by substrate structures or reaction conditions.3 This method ensured the direct sialylation of oligosaccharides and glycolipids in high yields,4,5,6 suggesting the potential of this method to rewrite the synthetic scheme of sialoglycans. Very recently, we demonstrated that macrobicyclic Kdo donors with α-configuration allowed for the full stereocontrol in the α-glycosidation. This method facilitated the stereoselective synthesis of the dimeric and trimeric Kdos found in lipopolysaccharide of pathogenic bacteria.

In this talk, I will share our recent results on the α-glycosidations of sialic acid and Kdo using bicyclic donors and their application to the synthesis of highly complex glycans and functionalized probes.

References
Biosketch of Speaker

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Prof. Hiromune Ando completed his PhD at Gifu University in 1999. After postdoctoral research at RIKEN and Gifu University in Japan, he was promoted to Assistant Professor at Gifu University in 2003. In 2008, he was concurrently appointed as Associate Professor at the Institute for Integration of Cell-Material Sciences (Kyoto University) and Gifu University. In 2017, he was promoted to Full Professor at the Center for Highly Advanced Integration of Nano and Life Sciences (Gifu University). In 2021, he has been appointed as the Vice Director of the Institute for Glyco-core Research (iGCORE) of Gifu University. His current research focus is on organic synthesis of complex glycoconjugates and chemical biology of glycan-enriched cell membrane domains.

Hiromune is a Director of the Japanese Society of Carbohydrate Research (JSCR) and a Board Member of the Japan Consortium for Glycobiology & Glycotechnology (JCGG). He was awarded JSCR Award for Young Scientist, Incentive Award for Young Scientist from the Society of Synthetic Organic Chemistry, and Encourage Award of Young Scientists from the Japan Society for Bioscience, Biotechnology and Agrochemistry. Recently, he received e-TCR Award 2018 from the Trends in Carbohydrate Research and 2019 Young Investigator Award from the Journal of Carbohydrate Chemistry. He is a member of the editorial board of Journal of Carbohydrate Chemistry.