Production of Carbohydrate Building Blocks from Red Seaweed Polysaccharides.

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The development of synthetic strategies towards natural oligosaccharides and their mimetics plays a pivotal role in biomedicinal chemistry. Agarans and carrageenans are abundant natural polysaccharides which are obtained in large scale by water extraction from a variety of red seaweeds. These galactans are low cost starting material for the preparation of useful and rare carbohydrate-based building blocks. The aim of this work was produce two sets of *C*-glycosyl aldehydes building blocks with L- and D-configuration from agarose and kappa-carrageenan. The partial acid-catalyzed mercaptolysis of the two galactans under mild conditions afforded agarobiose and carrabiose (ß-D-Gal*p*-(1→4)-3,6-anhydro-*aldehydo*-L- and D-galactose, respectively) derivatives. Complete depolymerization of agarose and kappa-carrageenan under harsher conditions produced 3,6-anhydro L- and D-galactose aldehyde derivatives. Chain shortening of these products via alditol formation and oxidative carbon-carbon bond cleavage furnished *C*-formyl α-L- and α-D-threofuranosides. Finally, a new procedure for the preparation of the 2,3-*O*-benzyl L-threofuranose was established by Baeyer-Villiger oxidation of the benzylated *C*-formyl α-L-threofuranoside. The main interest in the production of preparative amounts of L-threofuranose derivative lies on its use as starting material for non-natural nucleotides synthesis and subsequent generation of (2',3')-α-L-threose nucleic acid (TNA) sequences. In conclusion, the opposite stereochemistry of the 3,6-anhydro-galactose in the backbone of agarose and kappa-carrageenan enables the access to products which belong to L- and D-series of carbohydrates. This great potential offers a wide range of opportunities for studies in glycobiology and applications in biomedicinal chemistry.

Key words: Agarose; κ-carrageenan; *C*-glycoside building blocks.

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