GLYCOSYLATION OF INTERNAL SUGAR RESIDUES OF OLIGOSACCHARIDES CATALYZED BY α-GALACTOSIDASE FROM A THERMOTOLERANT FUNGUS *ASPERGILLUS FUMIGATUS*

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Purified α-galactosidase from a thermotolerant fungus *Aspergillus fumigatus* IMI 385708 was found to catalyze transgalactosylation reactions in the presence of high concentration of 4-nitrophenyl α-D-galactopyranoside (NPGal) as α-galactosyl donor. NPGal and monosaccharides (glucose, galactose, mannose, fructose, xylose and arabinose) served as poor glycosyl acceptors. Considerably higher yields of transglycosylation products were obtained with oligosaccharides composed of hexopyranosyl residues. In terms of yields, β-1,4-mannooligosaccharides corresponding to the main chain of galactomannan, the natural α-galactosidase substrate, were recognized as the best acceptors. The conversion to singly and doubly galactosylated products increased with degree of polymerization of oligosaccharides, reaching in total approximately 50 % with mannopentaose and mannohexaose. The α-galactosylation of mannooligosaccharides took place exclusively at the primary *O*-6 hydroxyl groups, which is in accord with the finding that β-1,4-xylooligosaccharides, lacking these groups, were not galactosylated. The galactosylation of mannopyranosyl residues in oligosaccharides was not random and involved preferentially internal sugar residues. The non-reducing-end terminal sugar residues, a common site for a glycosyl attachment catalyzed by other glycosidases, were not galactosylated. This is the first report of a unique glycosyl transfer reaction to internal sugar residues of oligosaccharides catalyzed by an α-galactosidase. High affinity to oligosaccharide acceptors also opens a way toward enzymatic α-galactosylation of polysaccharides and glycoconjugates, an environment-friendly way of modification of their physico-chemical and biological properties.

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Acknowledgment
Slovak Scientific Grant Agency is acknowledged for financial support of the research by a project VEGA No. 2/3079/23.