

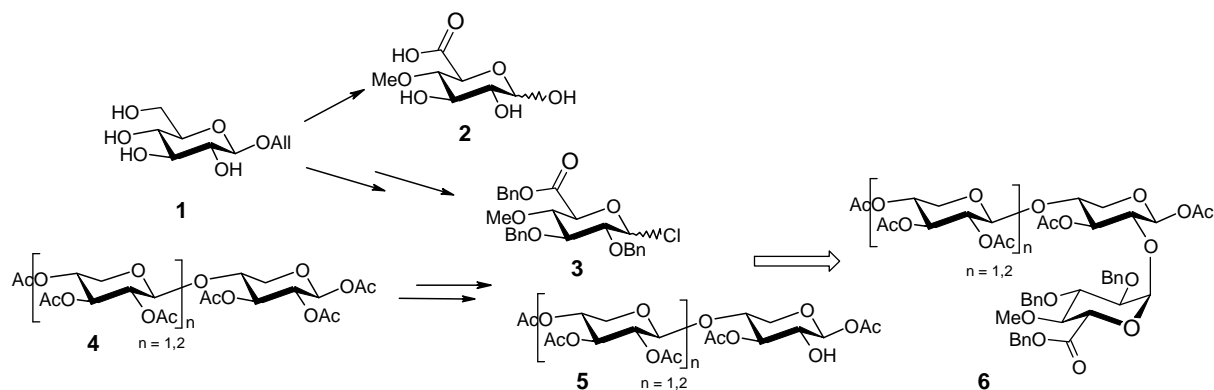
SYNTHESIS OF ACIDIC XYLOOLIGOMER MODEL COMPOUNDS

Wilhelm Herok,^a Beatriz Abad-Romero,^a Georg Sixta,^a Clemens Gruber,^a Herbert Sixta,^b and Paul Kosma^{a*}

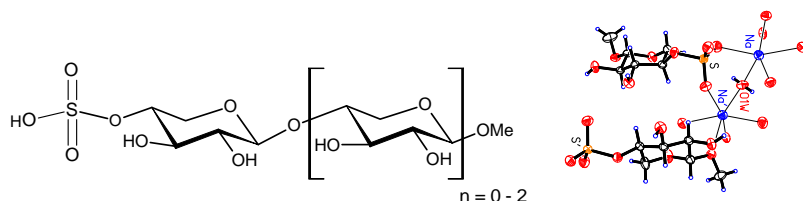
^(a) University of Natural Resources and Applied Life Sciences, Department of Chemistry, Muthgasse 18, A-1190 Vienna, Austria, * paul.kosma@boku.ac.at

^(b) Department of Forest Products, Helsinki University of Technology, Espoo 02015, Finland

4-O-Methyl-D-glucuronic acid (4OMeGlcA) is a frequently found constituent in hard-wood xylans such as beech wood xylan. In the context of utilizing low molecular weight fractions of xylooligomers obtained by degradation of xylans isolated from industrial process liquors, model compounds containing 4OMeGlcA residues were synthesized.¹ Starting from allyl β -D-glucopyranoside **1** and appropriate protecting group manipulation, methylation of OH-4 followed by TEMPO-oxidation / esterification eventually provided 4OMeGlcA glycosyl donor **3** as well as the free 4-O-methyl-D-glucuronic acid **2** after full deprotection, respectively. Orthoester formation of peracetylated xylooligomers and selective opening afforded the corresponding glycosyl acceptors to be coupled with glucuronic acid donors. Aldobio- and triouronic acids substituted at position 2 of the reducing end xylose unit display retarded degradation kinetics under alkaline conditions in contrast to model compounds carrying these substituents within the xylan chain.^{2,3}



Furthermore, sulfation of xylooligomers has been achieved at the distal 4-OH group of xylooligomers in good to fair yields using intermediate stannylene acetal formation followed by treatment with the SO_3 -dimethylamine complex. In addition, the 4-O-sulfate of methyl β -D-xylopyranoside could be crystallized as its sodium salt hemihydrate.⁴



¹ Abad-Romero, B.; Haltrich, D.; Potthast, A.; Rosenau, T.; Sixta, H.; Kosma, P. *Macromol. Symp.* **2006**, 232, 93.

² Oscarson, S.; Svalmberg, P. *J. Chem. Soc. Perkin Trans I* **2001**, 873.

³ Sartori, J.; Potthast, A.; Rosenau, T.; Hofinger, A.; Sixta, H., Kosma, P. *Holzforschung* **2004**, 58, 588.

⁴ Abad-Romero, B.; Mereiter, K.; Sixta, H., Hofinger, A.; Kosma, P. *Carbohydr. Res.* in press.

Acknowledgment: Supported by WOOD COMET