Carbohydrates in Interaction: When unity creates strength

François Portier, Jing Chen and Sami Halila
CERMAV, University Grenoble Alpes, Grenoble France

Polysaccharides are ubiquitous in Nature. They are present in every living organism such as plant and animal where they exhibit a very wide range of biological and mechanical functions acting primarily as energy source (starch and glycogen) or structuring materials (cellulose, chitin, glycolipids and proteoglycans). Cellulose is certainly one of the most abundant biopolymers found in nature, mostly as the main structural component of plant cell walls where they are embedded in a multi-component matrix in close interactions with hemicelluloses (xyloglucan, xylan etc.) and pectins. The strong affinity of xyloglucan (XG) to cellulose has attracted researchers for its application in cellulose-based materials where molecular weight, sugar composition and side-group structure of XG were defined as affecting the interactions.[1]

In the first part of the presentation, we will reveal that glycopolymers made of xyloglucan oligosaccharides side chains derived of tamarind seeds XG, termed as poly(XGO), efficiently interact with the high-surface area of bundles of rod-like cellulose nanocrystals (NCC) even if single subunits XGO are not able to bind to cellulose. We will focus on the synthesis, structural characterization and self-assembly properties of bottlebrush-like poly(XGO) containing different galactosyl substitution pattern. Then we will demonstrate their ability to interact with cotton NCC in aqueous medium using isothermal titration calorimetry (ITC) and polarized/depolarized dynamic light scattering (DLS).[2]

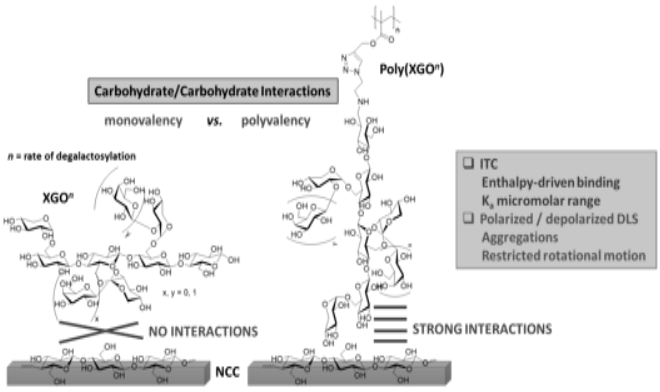

Figure 1. *Multivalent carbohydrate-carbohydrate interactions mimicking the plant cell-wall network.*

In the second part of the presentation, we will interest on glycochemistry at the interface with glycobiology. In fact, for the past 30 years, the carbohydrates have attracted intense interest because of their coating on cells of kingdom of life which provide internal and external cues for recognition, disease state, signal transduction, and more.[3] As a result, considerable progress has been made in method development for targeting carbohydrate-based diagnostic and/or therapeutic agents in the simplest way. For instance, to avoid pathogen adhesion to host cells, the design of glycomimetics of higher affinity was developed as synthetic ligands to hijack carbohydrate-binding pathogenic micro-organisms (bacteria, viruses). The shortest access to glycomimetics or (neo)glycoconjugates requires chemoselective ligations to the reducing-end anomeric position of carbohydrates which display an aldehyde function under its opening form. In carbohydrate chemistry, the aldehyde-condensation reaction is traditionally performed by amination with primary amines or with more reactive α-nucleophiles such as oxyamine or hydrazine derivatives. Interestingly, the Knoevenagel condensation using β-diketones is another very convenient method that leads to β-*C*-glycosides in one step directly from unprotected sugar.[4] However, it has been less developed in spite of its chemical and enzymatic stability and ring integrity of the terminal reducing sugar. In order to give it fresh impetus, we gain insight into the determinant structural parameters of β-*C*-glycosyl barbiturates interacting with carbohydrate-binding proteins, so called, lectins. Thus, we will present an expeditious synthesis of β-*C*-glycosyl barbiturates ligands of bacterial lectins starting from monomer design to multivalency.[5]

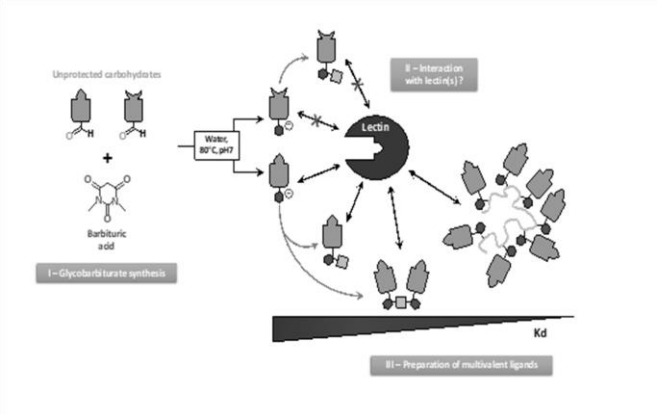

Figure 2. *β-C-glycosyl barbiturates ligands of bacterial lectins*

This work was supported by CNRS, Université Grenoble Alpes, the French National Research Agency in the framework of the "Investissements d'avenir" program Glyco@Alps (ANR-15-IDEX-02) and the Labex ARCANE (ANR-11-LABX-0003-01). We thank Emilie Gillon for her help in ITC measurements and ICMG FR 2607 platform (NMR, mass spectrometry) for the structural analyses.

References

1. Somerville C., Bauer S., Brininstool G., Facette M., Hamann T., Milne J., Osborne E., Paredez A., Persson S., Raab, T., Vorwerk S., Youngs H. *Science* 2004, 306, 2206−2211.
2. Chen J., Travelet C., Borsali R., Halila S. *Biomacromolecules*, 2017, 18 (10), 3410–3417.
3. Fernandez–Tejada A., Canada F.J., Jimenez-Barbero J. *Chem. Eur. J.* 2015, 21,10616 –10628.
4. J. A. Galbis, M. Avalos, J. L. Jimenez, J. C. Palacios. A facile synthesis of C-glycosylbarbiturates. Carbohydr. Res., 124 (1983) C15-C17.
5. Portier F., Imberty A., Halila S. *Article in redaction.*