Mobility-resolved NMR studies of Xylans from *Palmaria Palmata* cell wall

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The edible red seaweed *Palmaria Palmata* (L. Kuntze, Rhodophyta) produces in its cell wall blocks of (1→4)- and (1→3)-linked β-D-xylans in addition to cellulose and isolated β-(1→4)-D-xylan. This cell wall is supposed to contribute in specific mechanical properties playing an important role in its texture perception by the consumer and its ability to be processed. Interactions of the mix-linked xylans have been recently investigated by sequential solvent extractions and physico-chemical characterizations [1]. This work revealed that xylan was essentially held in the cell wall by hydrogen bonds. In order to further understand the mix-linked xylans contribution to the mechanical properties of the algal tissues, we investigated the chemical structure and interactions of these cell wall polysaccharides by liquid-like magic-angle-spinning (MAS) and cross-polarization MAS (CPMAS) solid-state ^{13}C NMR spectroscopy [2].

The liquid-like MAS and CPMAS ^{13}C NMR spectra of re-hydrated algal powder revealed the presence of β-(1→4)/ β-(1→3)-linked D-xylan with chemical shifts close to those observed for the solution ^{13}C NMR spectrum of the polysaccharide. Observation of mix-linked xylan in the liquid-like MAS ^{13}C NMR spectrum indicated that part of this cell wall polysaccharide is loosely held in the alga. The mix-linked xylan signals were observed in the CPMAS ^{13}C NMR spectrum of hydrated residues obtained after extensive extractions by NaOH or strong chaotropic solutions indicating strong hydrogen bonds or covalent linkages. $T_{1\rho}$ and T_2 relaxation times were measured on the alcohol insoluble residue (AIR) of the dry algal . $T_{1\rho}$ were found to be close or above 10 ms for the mix-linked xylan in the dry and hydrated state of AIR and indicated that the overall xylan chains remain rigid. Re-hydration of the mix-linked xylan induced a loosening of motions for the protons bounded to the C-1 and C4 carbons of the (1→4)-linked xylose supporting the re-organisation of the xylan chains under hydration involving hydrogen bonds between the (1→4)-linked xylose blocks.

References :

[1] Deniaud, E., Fleurence, J., Lahaye, M. *Interactions of the mix-linked β-(1→3)/β-(1→4)-D-xylans in the cell walls of Palmaria palmata (Rhodophyta).* J. Phycol. 2003, 39, 74-82

[2] M. Lahaye, C. Rondeau-Mouro, E. Deniaud, A. Buléon *Solid-state ^{13}C NMR Spectroscopy studies of xylans in the cell wall of Palmaria Palmata (L. Kuntze, Rhodophyta).* Carbohyd. Res. (accepted as : CAR2931)