

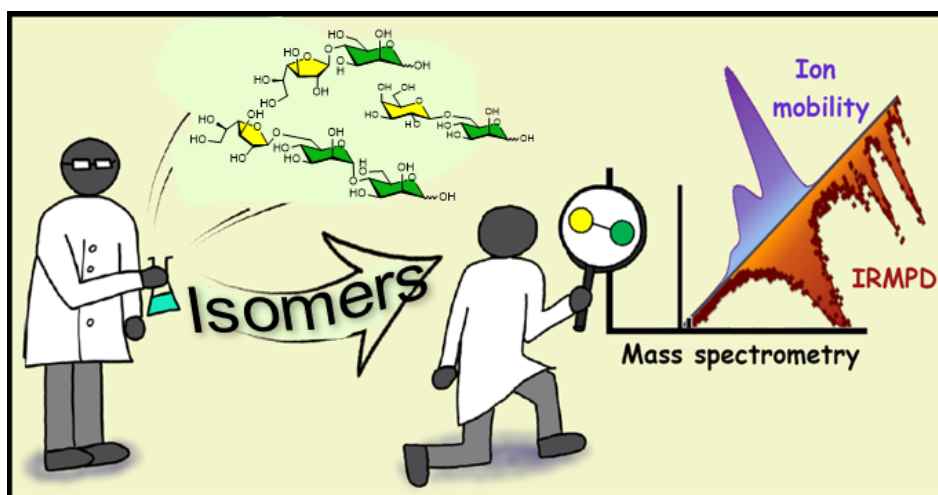
## Recent advances in the sequencing of rare lichenic carbo-hydrates using advanced mass spectrometry

Laurent LEGENTIL [1], Bénédicte FAVREAU [1], Louis-Philippe DAVID [1], Simon OLLIVIER [2], Oznur YENI [3], Françoise LE DEVEHAT [4], Isabelle COMPAGNON [3], David ROPARTZ [2], Vincent FERRIERES [1]

[1] Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR 6226, F-35000 Rennes, France, [2] INRAE, UR BIA, F-44316 Nantes, France, and INRAE, BIBS Facility, F-44316 Nantes, France, [3] Université de Lyon, CNRS, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Ma-tière, F-69622 Lyon, France, [4] Univ Rennes, CNRS, ISCR – UMR 6226, F-35000 Rennes, France.

laurent.legentil@ensc-rennes.fr

Lichens constitutes a unique symbiotic system of microalgae and a fungus. Till now, the lichen chemistry is mainly focused on secondary metabolites that represent 3 to 20% of the lichen dried weight while polysaccharides represent about 60% of the biomass. Interestingly, among identified polysaccharides, the galactomannans have attracted attention either as chemotaxonomic character to classify lichens or as bioactive compounds. The galactomannans are constituted mainly of a mannan backbone with different decorations depending of the symbiotic partners. One of the main one is the branching of a galactofuranose. Sugars in their furanose form are not usual in nature but of high interest as this motif can be found in numerous pathogenic microorganisms. Nevertheless, the detection of galactofuranose in Lichen's polysaccharides remains cumbersome, principally because of the sensitivity of galactofuranosides to mild hydrolysis conditions. To circumvent this problem, we have synthesized a library of di- and trisaccharides of galactomannans where the galactose adopted either the pyranose or the furanose form. This library served as standard for the implementation of a unique analytical flowpath relying on both Ion-mobility-Mass spectrometry analysis and Infra-Red Multiple-Photon Dissociation technics. It allowed to identify without any ambiguity the presence of the galactofuranose isomery as well as its regioisomery. Correlations between both techniques was established by molecular modeling to better understand the impact of conformational changes on physicochemical properties.



### Bibliographic references:

B. Favreau, O. Yeni, S. Ollivier, J. Boustie, F. Le Dévéhat, J. P. Guégan, M. Fanuel, H. Rogniaux, R. Brédy, I. Compagnon, D. Ropartz, L. Legentil, V. Ferrières, *J. Org. Chem.* 2021, 86, 6390-6405.  
J. S. Ho, A. Gharbi, B. Schindler, O. Yeni, R. Brédy, L. Legentil, V. Ferrières, L. L. Kiessling, I. Compagnon, *J. Am. Chem. Soc.* 2021, 143, 10509-10513.