LICHEN DATA BASE (LDB), A HIGH-RESOLUTION MASS-TANDEM LIBRARY FOR LICHEN METABOLITES

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Following works of J-P. Robiquet or orchil dyeing in 1829, studies on lichen chemistry afforded the first isolated metabolites, with a large input of German and Japanese chemists, culminating in the publication of S. Huneck & I. Yoshimura's "Identification of lichen substances" in 1996. This compendium summarized analytical and physico-chemical data for lichen molecules (TLC, NMR, LC, MS/MS and microcrystallization…) from the most influent authors on the subject. Nowadays the study of lichen chemistry is facilitated but remains generally associated with TLC standardized by C. F. & W. L. Culberson to vizualise the presence of the most common metabolites. The field thus remains underexplored in regards of the standards set in the era metabolomics where high-resolution LC-MS and NMR are commonplace. For instance, the efficiency of LC-MS as a quick dereplication method for complex mixtures is highly reliant on databases which are largely absent when it comes to lichens. Our aim is to renew an interest in lichen chemistry by providing the community with a modern dereplication standard for the LC-HRMS/MS analysis of lichens: a MS/MS database for lichen metabolites. A vast amount of lichen molecules was collected: 300 were graciously donated by the Berlin Botanical Museum from the Huneck' collection and completed by some molecules isolated in Rennes. All molecules were then analysed by HR LC-MS/MS. Data were manually curated and treated with bioinformatic tools used in metabolomics to serve as a public database for the community (https://gnps.ucsd.edu/ProteoSAFe/libraries.jsp). Technical validation was achieved through the dereplication of three lichen extracts by a Molecular Networking approach. This database should help streamlining the isolation of formerly unreported metabolites which are by far more numerous than the ones identified to now. This tool is also offering a versatile tool for a sharp chemical profiling of lichens.