**ISOTOPOLOGUE PROFILING FOR ANALYZING METABOLIC PATHWAYS IN INTACT LICHENS**

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Lichen secondary metabolites show important biological activities as well as pharmaceutical and chemotaxonomic potential. In order to utilize such substances of interest, detailed knowledge of their biosynthetic pathways is essential. Usnic acid is one of the best studied lichen metabolite with considerable and renewed interest for pharmaceutical and lifestyle applications. The biosynthesis of the bibenzofurane derivative is assumed to proceed via a polyketide pathway using two molecules of methylphloroacetophenone. Here, we have developed labeling experiments using the intact lichen *Usnea dasopoga* to further corroborate the pathway. Spraying of an aqueous solution of [U-13C6]glucose onto the thalli of the lichen afforded a specific pattern of multiple 13C-labeled isotopologs which confirmed a polyketide route *via* methylphloroacetophenone but not *via* phloroacetophenone. The proof-of-principle experiment also suggests that the method can be used in general to study metabolic pathways and fluxes in intact lichens.