Improving the annotation of unknown metabolites via integration of GCMS and LCMS metabolomics: A close look into the complexity of grapevine glycosides

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Abstract

Every grape cultivar has its own unique genetic characteristics, leading to the production of a different secondary metabolite profile. Volatile compounds in grapes are usually analyzed via GC-MS, while their glycosides are evaluated by indirect methods, after enzymatic or chemical hydrolysis.

A common feature of raw data from metabolomics experiments is that they cannot be immediately interpreted as relative concentrations of constituent compounds. A bottleneck here is the signal annotation, which is the process of tentatively associating the pseudospectra found with chemical structure. For the free volatiles, the annotation of large metabolomics dataset can be performed by an automatic pipeline that it is able to focus on hundreds of compounds simultaneously (Wehrens et al., 2014). However, there is scarcity of publications addressing the annotation of the glycosides, which makes the annotation of these compounds a challenging task.

In this study we present the molecular profiling of volatile compounds and their precursors in ten selected genotypes, including Vitis vinifera cultivars, American species and interspecific crosses. We tried to "gain from the complexity", since the difficult task of annotation of the glycosides was achieved through combined use of two orthogonal techniques, GC/MS and LC/HRMS, before and after enzymatic hydrolysis.

The results show that both free and glycosidically bound aroma precursors behave differently in each different grape cultivars and species. As many as 66 free aroma volatile molecules (originally existing and released after hydrolysis) were profiled through GC/MS analysis, while 15 glycosides were identified through LC/HRMS and correlation with GC/MS data.

Literature

Wehrens R., Weingart G., Mattivi F. (2014) MetaMS: An open-source pipeline for GC-MS-based untargeted metabolomics. Journal of Chromatography B, 966, 109–116.