## HPLC-MS/MS characterization of polyphenolic components of berries of different species of *Vaccinium* genus

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*Vaccinium myrtillus* berries (wild bilberry) are an important economic resource in various European regions, including Italian mountain areas, owing to their use as supplement of anthocyanins in the human diet. Berry anthocyanins are in fact recognized as anti-allergic, anti-inflammatory, antihypertensive, antimicrobial and anticancer molecules [1].

Recently, the presence of a different *Vaccinium* species, namely *V. gaultherioides*, has been increasingly observed in the zones traditionally populated by *V. myrtillus*, such as Tuscan Apennines. The phenotype of *V. gaultherioides* berry is very similar to the one of *V. myrtillus* and the two berries can be confused by the harvesters involved in the production chain of transformed bilberry. This aspect is potentially awkward since no data regarding the primary and secondary metabolic profiles of *V. gaultherioides* berries, including anthocyanins, are reported in literature.

For this reason, the polyphenolic composition of *V. myrtillus* and *V. gaultherioides* berries has been comparatively investigated using liquid chromatography coupled with mass spectrometry. Different stationary phases (e.g. C18 and pentafluorophenyl) and particle sizes (2.6 and 1.7  $\mu$ m) have been tested in order to enhance the chromatographic selectivity. Target tandem and non-target high-resolution mass spectrometric approaches have been investigated.

Furthermore, antiradical (DPPH method) and antioxidant (FRAP method) activities have been determined for the two berry species.

The results showed that the two species exhibit very different abundances of phenolic substances and antiradical/antioxidant activities. More in detail, *V. myrtillus* fruits had much higher contents of phenolic compounds and antiradical/antioxidant activities than those of *V. gaultherioides*. The anthocyanin profiles of the two species was different as well, being *V. myrtillus* and *V. gaultherioides* berries dominated by delphinidin/cyanidin glycosides, and by malvidin derivatives, respectively.

Based on these results, it is of paramount importance to carefully distinguish between the two species during the harvesting activities.

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