

# Liquid chromatographic/electrospray ionization quadrupole/time of flight tandem mass spectrometric study of polyphenolic composition of different *Vaccinium* berry species and their comparative evaluation

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**Abstract** Ultra-high-performance liquid chromatography coupled with high-resolution quadrupole-time of flight mass spectrometry with both negative and positive ionization was used for comprehensively investigating the phenolic and polyphenolic compounds in berries from three spontaneous or cultivated *Vaccinium* species (i.e., *Vaccinium myrtillus*, *Vaccinium uliginosum* subsp. *gaultherioides*, and *Vaccinium corymbosum*). More than 200 analytes, among phenolic and polyphenolic compounds belonging to the classes of anthocyanins, monomeric and oligomeric flavonols, flavanols, dihydrochalcones, phenolic acids, together with other polyphenolic compounds of mixed structural characteristics, were identified. Some of the polyphenols herein investigated, such as anthocyanidin glucuronides and malvidin-feruloyl-hexosides in *V. myrtillus*, or anthocyanidin aldopentosides and coumaroyl-hexosides in *V. uliginosum* subsp. *gaultherioides* and a large number of proanthocyanidins with high molecular weight in all species, were described for the first time in these berries. Principal component analysis applied on original LC-TOF data, acquired in survey scan mode, successfully discriminated the three *Vaccinium* berry species investigated, on the basis of their polyphenolic composition, underlying one more time the fundamental role of mass spectrometry for food characterization.

**Keywords** Polyphenols · Flavonoids · *Vaccinium* species · Liquid chromatography · High-resolution mass spectrometry · Principal component analysis

## Introduction

The consumption of berries (e.g., blackberry, bilberry, blueberry, and cranberry) is considered an important contribution to healthy diets, owing to the various classes of phenolic compounds contained in large quantities in these fruits [1]. In fact, the class of phenolic compounds comprises a very high and increasing number of bioactive compounds [2], which are suggested to provide important health-protecting attributes such as anti-inflammatory, antihypertensive, antimicrobial, and anticancer properties [3].

Among the different berry species, *Vaccinium myrtillus* is the wild bilberry native to mountain areas of Northern and Central Europe, widely diffused also in Italian Alps and Apennines. In these zones, the increasing presence of a different spontaneous *Vaccinium* species, recently identified through genetic analyses as the *Vaccinium uliginosum* subsp. *gaultherioides* (locally named “false bilberry”), has been recently observed [4]. The cultivation and commercialization of *Vaccinium corymbosum* berries (i.e., the blueberry) is also widespread in the same area.

*V. myrtillus* is one of the richest fruit in polyphenols, with particular regard to anthocyanins [5] and is therefore considered a “functional food” [6]. Accordingly, *V. myrtillus* berries are largely consumed both as fresh fruits and processed products, such as juices and dietary supplements.

Many researches focusing on the determination of selected anthocyanins were carried out on bilberries from different European areas [7–11]. Interestingly, the composition of the

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