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METHYL SALICYLATE GLYCOSIDES IN SOME ITALIAN VARIETAL WINES

Silvia CARLIN (a)

Domenico Masuero^a, Graziano Guella^a, Urska Vrhovsek^a, Fulvio Mattivia^{a,b}

a) Department of Food Quality and Nutrition, Research and Innovation Centre, Fondazione Edmund Mach (FEM), Via E. Mach, 1 38010 S. Michele all'Adige, TN, Italy

b) Centre for Agriculture, Food and the Environment (C3A), University of Trento, San Michele all' Adige, Italy

c) Bioorganic Chemistry Laboratory, Department of Physics, University of Trento, Trento, Italy.

Email: silvia.carlin@fmach.it

Glycosides are ubiquitous plant secondary metabolites consisting of a non-sugar component, called an aglycone, attached to one or more sugars. One of the most interesting aglycones, found in grapes and in wine, is methyl salicylate (MeSA). MeSA is an organic ester naturally produced by many species of plants, particularly wintergreens. It is synthesised from salicylic acid, a phytohormone that contributes to plant pathogen defence and some of MeSA glycosides are expected to substitute aspirin due to their long-term effects and fewer side effects. To date nine different methyl salicylate glycosides from plants have been reported (Mao *et al.*, 2014). These methyl salicylate glycosides are mainly spread over the genera Gaultheria, Camellia, Polygala, Filipendula and Passiflora. From the sensorial point of view, methyl salicylate has a balsamic-sweet odour that is known as "Wintergreen oil".

Methyl salicylate was found in *V. riparia* grapes by (Schreier & Paroschy, 1980) and in *V. vinifera* sp. (Cabaroğlu *et al.*, 1997; Versini, Moser, & Carlin, 2005) and in the Frontenac interspecific hybrid (Mansfield, Schirle-Keller, & Reineccius, 2011). We found that the methyl salicylate glycosides content in Verdicchio wines and in some genetically related varieties (Trebiano di Soave and Trebbiano di Lugana) was very high. In order to understand which glycosides were present in wine, the methanolic extract of Verdicchio wine after SPE was injected into a UPLC-Q-TOF-HDMS, extract of different plants particularly rich in such glycosides, were also injected. We confirmed, using pure standards, the existence in wine of two glycosides: a MeSA 2-O-β-D-glucoside and a MeSA 2-O-β-D-xylopyranosyl(1-6) β-D-glucopyranoside (gaultherin), we also tentatively identified, for the first time in wine, other diglycosides: MeSA 2-O-α-L-arabinopyranosyl(1-6)-β-D-glucopyranoside (violutoside) and MeSA 2-O-β-D-apiofuranosyl(1-6)-β-D-glucopyranoside (canthoside A), a MeSA 2-O-β-D-glucopyranosyl(1-6)-O-β-D-glucopyranoside (gentiobioside) and a MeSA-2-O-α-L-rhamnopyranosyl(1-6)-β-D-glucopyranoside (rutinoside). Some of this glycosides have been isolated from Gaultheria leaves and NMR analysis are underway to provide detail information about the structure. In order to understand if these glycosides are a "peculiarity" of Verdicchio wines and its homologous, 40 different white wines were analysed. The range of concentration for the sum of this 6 MeSA glycosides was very variable from 0 to 300 µg/L. As the olfactory threshold of this compound is between 50 and 100 µg/L, it is suggested that methyl salicylate contributes to the balsamic scent in old Verdicchio wines.

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