

BOOK OF ABSTRACTS



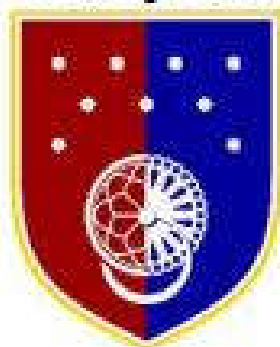
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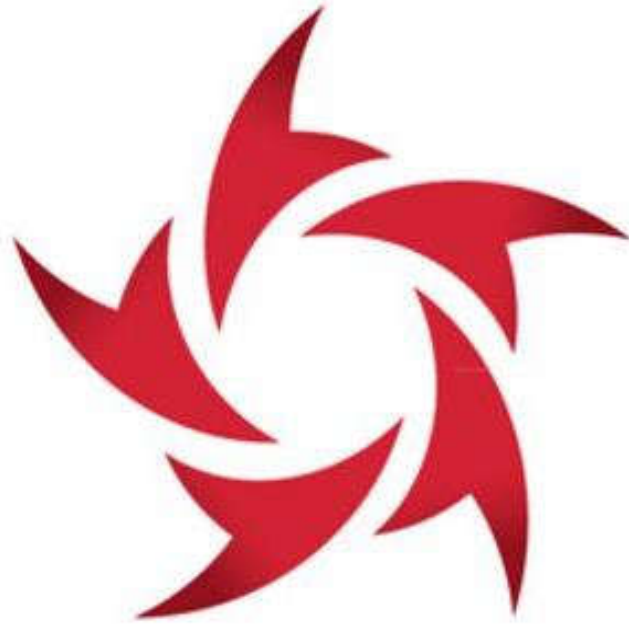
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IDENTIFICATION OF ANTHOCYANINS AND ANTHOCYANIN-DERIVATIVES IN VRANEC WINES DURING AGING

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This study aimed to characterization of the major anthocyanins (3-monoglucosides, 3-acetylglucosides, and 3-coumaroylglucosides), pyranoanthocyanins and hydroxyphenyl-pyranoanthocyanins in Vranec wines during aging of three years. The HPLC-DAD-ESI-MSⁿ technique was used for identification of the analytes. Anthocyanins presented mass spectra characterized with two signals, molecular ion M⁺ and fragment ions [M-162]⁺, [M-204]⁺ and [M-308]⁺ which resulted from the loss of glucose, acetylglucose and p-coumaroylglucose groups, respectively. The pyranoanthocyanins derived from pyruvic acid, called 10-carboxy-pyranoanthocyanins or A-type vitisins, such as 10-carboxy-pyranomalvidin-3-glucoside (vitisin A), 10-carboxy-pyranomalvidin-3-acetylglucoside (acetyl-vitisin A) and 10-carboxy-pyranomalvidin-3-p-coumaroylglucoside (p-coumaroyl-vitisin A) were identified according to their molecular ions (M⁺) and the characteristic fragment ([M+H]⁺ = m/z 399). B-type vitisins, resulting from cycloaddition reaction between anthocyanins and acetaldehyde, including pyranomalvidin-3-glucoside (vitisin B) and pyranomalvidin-3-acetylglucoside (acetyl-vitisin B), presented molecular signals M⁺ at m/z 517 and 559 and producing a fragment ion at m/z 355 by loss of glucoside (162u) and acetylglucoside (204u) groups, respectively. Moreover, six hydroxyphenyl-pyranoanthocyanins produced in the reaction of caffeic acid (10-(3''',4'''-dihydroxyphenyl)-pyranomalvidin-3-glucoside, 10-(3''',4'''-dihydroxyphenyl)-pyranomalvidin-3-acetylglucoside and 10-(3''',4'''-dihydroxyphenyl)-pyranomalvidin-3-p-coumaroylglucoside) and p-coumaric acid (10-(4'''-monohydroxyphenyl) derivatives of pyranomalvidin-3-glucoside, pyranomalvidin-3-acetylglucoside and pyranomalvidin-3-p-coumaroylglucoside) with different anthocyanins, were detected in the wines.

Keywords: anthocyanins, pyranoanthocyanins, hydroxyphenyl-pyranoanthocyanins, Vranec wine, HPLC-DAD-ESI-MSⁿ