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MALDI-TOF AND HPLC-DAD-ESI/MS IDENTIFICATION OF PHENOLIC COMPOUNDS IN MACEDONIAN WINES AND GRAPES

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Abstract

Phenolic compounds are one of the major quality parameters in the grape and thus in the resulting wine. They contribute to sensory characteristics of wines, particularly color and astringency, and possess a wide range of biochemical and pharmaceutical effects, including antioxidant, antimutagenic, antimicrobial and anticarcinogenic effects. These constituents can be divided into two groups: non-flavonoids (hydroxybenzoic and hydroxycinnamic acids and stilbens) and flavonoids (anthocyanins, favonols and flavan-3-ols).

MALDI-TOF and HPLC-DAD-ESI/MS methods were developed for simultaneous identification of phenolic acids, flavonols, anthocyanins, flavan-3-ols and stilbenes in Macedonian wines and grapes.

A rapid MALDI-TOF method was developed for wine and grape fingerprinting without preparation of the samples for identification of anthocyanins introducing a new matrix, fullerene C_{70}. Different MALDI matrices were tested: α-cyano-4-hydroxycinnamic acid (CHCA); 2,5-dihydroxy benzoic acid (2,5-DHB); sinapic acid (SA); fullerene (C_{70}) and measurements of some samples without matrix were done. It was found that fullerene can be used for identification of anthocyanins in wines and grapes and the sandwich method with this matrix was applied for all sample measurements.

A simple HPLC-MS method was applied for simultaneous identification of phenolic compounds present in wine and grape samples. Analyses were performed on a C18 column with gradient elution using a binary mobile phase consisting of 1 % acetic acid in water and 1 % acetic acid in methanol. Identification of the components was based on retention times, UV-Vis and mass spectra by comparison with a few commercial standards. The optimized HPLC method was used for phenolics analysis in grapes and wines from Vranec, Merlot, Chardonnay and Smederevka varieties (harvest 2007).

The obtained results confirm the great utility of ESI-MS coupled with HPLC for simultaneous analysis of non-flavonoid and flavonoid compounds in wine and grape samples, since coelution is not a problem in so far as they have different molecular masses.

Keywords: phenolic compounds, wine, grape, MALDI-TOF, HPLC-DAD-MS, phenolic acids, flavonols, anthocyanins, flavan-3-ols, stilbens, identification