

Classification of NMR spectra collected on wines added with anthocyanins from grape and black rice

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During wine-making of red wine, different phenolic compounds are extracted from the skin of grape berries and transferred into the must. Among them, the anthocyanins are particularly important being the substances mainly responsible for the colour of red wines, in which are contained in variable concentration, i.e. 100÷1500 mg/L¹. The degree of extraction of anthocyanins, and consequently the colour of the produced wine, are influenced by several factors, such as grape variety, soil composition, ripening conditions, viticulture techniques and wine-making methods.

In the Italian oenological industry, the common practice used to naturally increase the colour of red wines consists in blending them with a wine very rich in anthocyanins, namely Rossissimo dell'Emilia. On the Asian market, on the other hand, anthocyanins extracted by black rice are used as correctors for wine colour, as evidenced in more recent times. This probably happens because the extraction of anthocyanins from black rice is a very advantageous practice since the total content of anthocyanins in the whole seed is 0.16%¹ on average, and anthocyanins are mainly located in the outer parts of the seed, that are usually removed as refuse.

From the toxicological point of view, the use of anthocyanins from black rice for increasing red wines colour does not produce negative effects of health, however, in many countries – also in Italy – this custom is considered a food adulteration.

Currently, the total anthocyanins content in wine is determined by UV-Vis spectroscopy that, nevertheless being a rapid and reliable method, it does not permit the speciation of anthocyanins, which are present with different relative ratios in different plants. Another technique able to characterise the anthocyanic component of wines in a more specific way should be NMR spectroscopy².

In this work, were prepared two series of samples starting from five different kinds of wines: the first series was prepared by adding to each wine different amounts of Rossissimo dell'Emilia, while the second series was prepared by adding different amounts of black rice anthocyanins solution until the desired colour index is reached. Then, one-dimensional ¹H NMR spectroscopy was used to analyse the set of 35 samples in double.

After the explorative analysis of normalised, meancentered and smoothed signals by PCA, only the spectral region between 6.5 and 9.5 ppm was retained for the successive classification. Initially, PLS-DA was used as classification method to distinguish wine samples added with Rossissimo or with black rice anthocyanins solution, then also variable selection/classification methods were applied, that are iPLS-DA and WPTER³.

1. *J. Food Drug Anal.*, 6 (1998) 729
2. *Anal. Chim. Acta*, 458 (2002) 77–84
3. *Chemom. Intell. Lab. Sys.* 57 (2001) 97-119