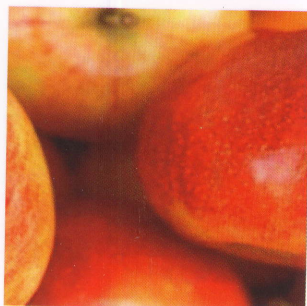
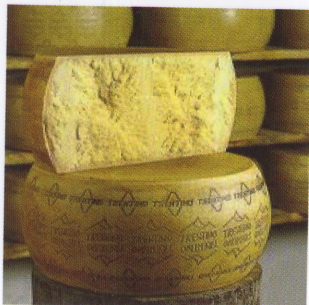




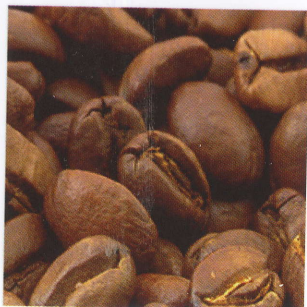
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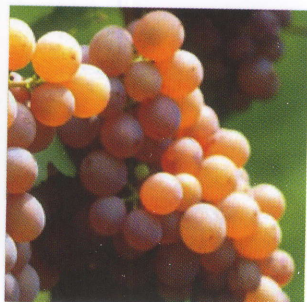


BOOK OF ABSTRACTS



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P.94 - Elemental and isotopic profiling: a tool for distinguishing the botanical origin of oenological tannins

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Summary: Oenological tannins are natural products extracted from different botanical sources such as galls, wood and grape tissues. Forty-four samples of commercial tannins from 7 different and known botanical sources were analysed to determine the mineral profile and isotopic ratio $^{13}\text{C}/^{12}\text{C}$, using ICP-MS and IRMS respectively. Canonical discriminant analysis performed using these combined approaches made it possible to determine the botanical origin of commercial tannins, achieving good separation between samples and 100% correct reclassification.

Keywords: *Oenological tannins; ICPMS; IRMS*

Introduction

According to the International Oenological Codex of the O.I.V., oenological tannins are natural products extracted from different botanical sources. In winemaking these products are used mainly as clarification/fining agents for wines and musts, but the European authorities also recognise the role of tannins as flavourings and food ingredients. These polyphenolic compounds can have effects on wine structure, colour, flavour and astringency and could act as antioxidant and antimicrobial agents [1]. The characterisation and identification of tannins is useful in terms of official checks and fulfilment of winemakers' requirements. The ultraviolet absorption spectrum, content of specific phenolic compounds and polyalcohol and monosaccharide composition were used to characterise and distinguish oenological tannins according to their botanical origin [2-5]. Determination of mineral profile and stable isotope ratios, together with proper statistical processing has already been shown to be very effective in differentiating the geographical and/or botanical origin of different products, such as tomatoes, cheese, cereal and coffee [6-9]. This work, for the first time to the best of our knowledge, investigates the possibility of determining the botanical origin of commercial tannins on the basis of mineral profile and analysis of the isotopic ratio $^{13}\text{C}/^{12}\text{C}$.

Experimental method

Forty-four samples of commercial oenological tannins of known botanical origin were collected. In detail, 15 samples were from oak, 15 from grapes (7 from seeds and 8 from skin), 3 from gall, 4 from quebracho, 4 from fruit trees and 3 from chestnut. The tannins were mineralized with ultrapure HNO_3 in closed vessels using a microwave digester (UltraWAVE, Milestone, Italy; max temperature 240°C). Analysis of Li, Be, B, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Tm, Yb, Re, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th and U was carried out using an ICP-MS (Agilent 7500ce Agilent Technologies, Japan) equipped with an Octopole Reaction System for removal of the principal polyatomic interferences. The $^{13}\text{C}/^{12}\text{C}$ ratio was directly measured using an IRMS (DELTA V, Thermo Scientific, Germany) after total combustion in an elemental analyser (EA Flash 1112, Thermo Scientific or Vario EL III, Elementar Analysensysteme GmbH). The isotope values were expressed in $\delta\text{‰}$ against the international standard Vienna-Pee Dee Belemnite (V-PDB).

Results

Tannins from oak were characterised by a high Tl content and low content of V, Ga and rare earths; tannins from gall showed a low Li, Na and Cu content, while those from chestnut had a high content of Al, Ti, Mn, Co, Ag, Cd, Ba, Pb, Th and rare earths. Quebracho tannins were characterised by a high Li, Cr, Sr and Hg content. Tannins from grape seeds had a high Ge content and low content of Mg, Co, Ni, Mn and Cd, whereas samples from grape skin had a high Mo, Sn, Sb, Re and U content. Tannin from grape tissues showed a high P, K, As and Cu content and a low Be content. To assess efficiency in terms of discriminating the botanical origin of tannins, principal component analysis was performed using all the parameters analysed. Only elements with factor loadings of > 0.5 in at least one of the first three principal components were used to perform canonical discriminant analysis (13C/12C, Li, Be, B, Na, Mg, Al, Ca, Ti, V, Mn, Fe, Co, As, Se, Rb, Sr, Y, Mo, Pd, As, Cd, In, Sn, Sb, Cs, Ba, Tl, Pb, Th and U, standardised data). The combination of the first 2 canonical variables accounted for 83% of variability, assuring good discrimination of the samples in the 7 botanical groups, and all the samples were correctly re-classified (Figure. 1).

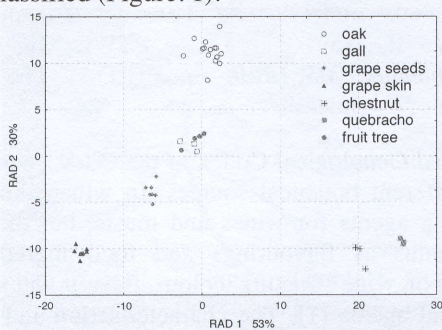


Figure.1 Scatter plot of the first two canonical variables in canonical discriminant analysis of the elemental and isotopic composition of tannins from 7 botanical sources

Conclusion

Using the “classic” approach based on analysis of sugars suggested by the O.I.V. the ability to differentiate the botanical origin of tannin in 82% of samples has already been proved [4]. More recently, an approach which coupled sugar and phenol content made it possible to correctly reclassify 93% of tannins [5]. The results achieved with joint use of the mineral profile and 13C isotopic ratio proved the effectiveness of these approaches in terms of providing practical support for assessing the real origin of these expensive food coadiuvants.

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