

"Isotopic model for detecting original wine product"

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Abstract

This paper presents a study concerning the stable isotopic fingerprint (D, ^{18}O and ^{13}C) of some wines varieties (Xinomavro, Agiorgitiko, Moschato, Syrah) obtained from different regions of Greece. These wines were obtained from different vineyards having a significant role in the wine market: Amyntaio, Orestiada located in Northern Greece and Nemea located in Southern Greece. From the $\delta^{13}\text{C}$ and D values we conclude that all the studied wines were authentic. The variations on the $\delta^{18}\text{O}$ were well correlated with the different climatic zones of the regions. Specifically, the North and North-East regions of Greece (Amyntaio and Orestiada respectively) showed oxygen values in the range of -1.3‰ to 5‰ and -1.0‰ to 5.5‰ while the South regions of Greece (Nemea) showed values in the range of 2.5‰ to 6.1‰.

Introduction

Food authenticity is an important subject in the food industry. Laws are issued to protect the origin and brand in the expanding global markets since prestige and well known products are subject to fraud like adulterations and mislabeling practices. Furthermore, the needs of globalization and of the mass production have alienated the food products from their origin and their traditional production methods that both influence the final food product. Especially in the wine industry, where the value of the product is directly related to the origin and the year of wine grape production, it is essential to develop methods that could potentially verify the origin of the product and assess its quality according with the relevant laws of alcohol production in order to protect the consumers and the legitimate wine industries.

One of the most versatile and important methods of monitoring, determination of quality, authenticity and origin are stable isotopes (isotopes D, ^{13}C and ^{18}O) dating back in the early seventies and further developed by the use of radiocarbon ^{14}C and radiogenic isotopes Sr and Nd. Stable isotope ratio analysis of wine and isotope ratio mass spectrometry are official methods in the European Union for the detection of chaptalization, addition of water, sweetening with sugar, and authentication of geographic origin and year of harvest.

Wines are a relative easy food product to manipulate and the need to develop even more sophisticated methods to detect potential falsifications is essential. In this context,

adulteration practices can be detected more simply if the geographic origin of the wine is ascertained. A method to achieve this geographical origin determination is by investigating the relation of the water inside the wine with the water of the same geographic region. In this paper we review the available data from spring water of specific wine producing regions of Greece and compare with the water content of the wines of these specific wine producing regions.

The isotopic contents of the water of wine present a complicated influence pattern on various environmental, natural and anthropogenic elements. The main natural influences in the isotopic composition of the water are the average rain-out history of the air masse (Merlivat & Jouzel, 1979; Rozanski, Sonntag, & Munnich, 1982; Bowen & Revenaugh, 2003), the water-rock interaction, the transit time, the evaporation processes and the recharge elevation of the water captured for irrigation. This water is then transferred in the grapes. Contrary, if irrigated grapes are used, the water precipitation may be significantly different. Taking all the above into account for specific wine producing areas will in principle reveal a different pattern in the isotopic content of $\delta^{18}\text{O}$ - $\delta^2\text{H}$ in the water of vegetation, vine grapes and wine, and hopefully it may reflect the area from where the wine product has originated (its geographical origin).

The environmental influence of the final pattern of the wine water is mainly due the opening and closing stomata in order to adapt the phyton to the water availability from atmospheric humidity and soil moisture. During the plant maturation different enrichments in the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ of water of phytons and fruits will demonstrate the influence of the environmental conditions. The evapotranspiration taking place during this period is considered a factor of isotopic fractionation; this process causes enrichment in heavy isotopes of both oxygen and hydrogen of water of phyton and fruits. Furthermore, it has been proven that the climate factors influence the $\delta^{13}\text{C}$ value of wine ethanol, [$\delta^{13}\text{C}$ (VPDB) value from -20‰ to -35‰ versus PDB (Pee-Dee Belemnite, SC, USA)] in greater extent than the different atmospheric CO_2 concentrations (which is the source of carbon in plants).

The stable isotopes of carbon ($\delta^{13}\text{C}$) can also be used to document adulteration of wine. This adulteration takes place through the addition of sugar (beet or cane sugar). This operation increases the alcohol and/or sugar content of the beverage via the fermentation mechanism performed by yeasts. Plants use three different photosynthetic

pathways: C3, C4, and CAM. The photosynthetic pathway is distinguished with characteristic range of $\delta^{13}\text{C}$ values: C4 (Hatch-Slack, C4-dicarboxylic acid path-way) plants generally range from -9% to -19% (O’Leary, 1988) while for C3 (Calvin cycle) plants typically range from -20% (open areas exposed to water stress) to -35% (closed canopy) (O’Leary, 1988). The third photosynthetic pathway called CAM presents $\delta^{13}\text{C}$ values between the end-members of C3 and C4 types.

Material and methods

In this study, hydrogen, oxygen and carbon isotopic compositions of 50 wines available on the Greek market were determined and a first isotopic characterization of Greek wines is presented. We investigate the role of the environment conditions in the control of the stable isotope ratios [ethanol ($^{13}\text{C}/^{12}\text{C}$) and wine water contents ($^{18}\text{O}/^{16}\text{O}$)] of wines produced in different wine-producing areas of Greece.

Wine samples were obtained from, Amyntaio, Nemea and Evros-Orestiaida area. Specifically, we have analyzed wine samples of “Agiorgitiko” (Nemea), “Tannat” (Amyntaio), “Syrah” (Amyntaio), “Xinomavro” (Amyntaio) and “Moschato” (Evros-Orestiaida). In order to correlate with the local water sources, rain samples were also collected from the above areas.

All stable isotopic analyses were performed in Stable Isotope Unit of Nanoscience & Nanotechnology Institute in N.C.S.R. Demokritos (Athens, Greece). Stable isotope analysis in Greek wines, wine water, meteoric and ground waters were carried out in Stable Isotope Unit of Nanoscience & Nanotechnology Institute in N.C.S.R. Demokritos (Athens, Greece) on a continuous flow Finnigan DELTA V plus (Thermo Electron Corporation, Bremen, Germany) stable isotope mass spectrometer according to the procedures described by Hilkert and Avak, 2004 and Duhr and Hilkert, 2004.

The results are expressed in standard delta notation (δ) as per mil (‰) deviation from the standard V-SMOW as: $\delta = ((R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}) * 1000$ where R_{sample} and $R_{\text{standard}} = ^{18}\text{O}/^{16}\text{O}$ or $^{13}\text{C}/^{12}\text{C}$ ratios of sample and standard respectively.

All measurements were carried out according to laboratory standards that were periodically calibrated based on the international standards recommended by the IAEA.

In the following table we present the resulting values for the isotopic values of $\delta^{18}\text{O}$ ‰, $\delta^{13}\text{C}$ ‰ and D/H ppm. From the values of the $\delta^{13}\text{C}$ (column three in the table) we observe an isotope enrichment in the North-South direction of Greece, which was previously reported by some authors for olive oils (Angerosa *et al.*, 1999; Bréas *et al.*, 1998)

| | $\delta^{18}\text{O}$ ‰ | $\delta^{13}\text{C}$ ‰ | D/H ppm |
|-----------------|-------------------------|-------------------------|------------|
| Orestiaida (NE) | -1.0 to 5.5 | -27 to -25.3 | 97 to 104 |
| Amydaio (N) | -1.3 to 5.0 | -29.4 to -26.1 | 98 to 104 |
| Nemea (S) | 2.5 to 6.1 | -26.2 to -24.7 | 100 to 106 |

Results-Discussion

In order to check whether different climatic zones of Greece have an influence on stable isotope values ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$), we analyzed wines obtained from Amydaio (Macedonia, Northern Greece), Nemea (Peleponesus, Southern Greece) and Evros-Orestiaida (North-Eastern Greece).

values with larger variations verifying the warmer and drier conditions than those of Amydaio where the conditions are cooler and the precipitation episodes more frequent and constant.

The differences observed for the $\delta^{18}\text{O}$ values were certainly a result of different weather conditions in the studied areas. Between the North (Amyntaio, Macedonia, Northern Greece) and North East side (Orestiaida, Evros, Eastern Greece) and the south (Nemea, Peleponesus, Southern Greece) side of the country, the difference in temperatures is about 5°C , but the differences related to precipitation were more relevant, ranging from about 1400 mm annual average in the north side to less than 700 mm annual average in the south side of the country. These climatological differences mainly influenced the $\delta^{18}\text{O}$ values, with the variation of the more positive of $\delta^{13}\text{C}$ between the Nemea area (-24.7%) and the Amyntaio area (-26.1%) being much higher.

Furthermore, the values of the D/H ranged between 97ppm and 106ppm and they are consistent with the international corresponding values given for wine [98ppm to 108ppm] indicating that the tested wines were authentic.

As a final observation, the $\delta^{18}\text{O}$ values were compatible with the values of the local waters tested, indicating the origin of the wines.

Conclusions

Moreover, Nemea wines present slightly more positive

Hydrogen, oxygen and carbon isotopic compositions of 50 wines available on the Greek market were determined and a first isotopic characterization of Greek wines is presented. We investigate the role of the environment conditions in the control of the stable isotope ratios [ethanol ($^{13}\text{C}/^{12}\text{C}$) and wine water contents ($^{18}\text{O}/^{16}\text{O}$)] of wines produced in different wine-producing areas of Greece. The $\delta^{18}\text{O}$ values correlated the studied wines with the local water sources and a North-South isotopic enrichment was established. From the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values the wines were proven authentic.

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