Assessing the isotopic fingerprint of ethanol from Transylvanian distillates

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Abstract

Romania has an old tradition in production of fruit spirits. The authentication of distillates is an important research field because their composition has a considerably higher variation than the one of beer or wine, whereas numerous raw materials are permitted in production process. Isotopic fingerprints of ^{2}H and ^{18}O were determined by high temperature pyrolysis system coupled to an isotope ratio mass spectrometer (IRMS). The data set consisted in 50 fruit distillates, coming from Transylvania, Romania, produced from plums, apples, pears, apricots and quinces. The variation range was between 7.9 ‰ and 21.7 ‰ for $\delta^{18}O$, and between -228.0 ‰ and -160.2 ‰ for $\delta^{2}H$, respectively. Also, $\delta^{13}C$ of ethanol from fruit spirits was determined. The ^{13}C fingerprint ranged between -28.0 ‰ and -18.6 ‰.

Background

Nearly all Romanian traditional strong drinks are made from fruits, which technically makes them a “brandy”. The term “brandy” refers to any alcohol made by fermenting and distilling fruit. The most appreciated fruits which are used for the spirits production in Romania, and particularly in Transylvania region, are plums. Fermenting and twice distilling plums results the nationally famous drink “tuica”, having 24 – 65 % alcohol volume. It is estimated that over 75% of all the plums harvested in Romania are used to make “tuica”.

“*Palinca*” is another traditional Romanian alcoholic beverage obtained exclusively by alcoholic fermentation and distillation of a fleshy fruit or a mixture of fruits, except plums.

Experimental

- To determine $^{2}H/^{1}H$ and $^{18}O/^{16}O$ isotope ratios, the first performed step consisted in the obtainment of the ethanol from fruit spirits distillates.
- Extraction of ethanol was performed using a Cadiot spinning band column.
- The remaining water was trapped by preserving the distillate for 48 h on a molecular sieve, 3Å (beads, 8-12 mesh, Sigma-Aldrich), as was previously described an discussed in the literature by Perini & Camin (2013).
- In the next step, a high-temperature pyrolysis system of the elemental analyzer (Flash EA 1112 HT) coupled to an isotope ratio mass spectrometer (Delta V Advantage, Thermo Scientific) was used.
- The working standards were H_2 and CO, which were calibrated versus Vienna Standard Ocean Mean Water (VSOMW) international standard ($\delta^{2}H_{VSMOW}$ = 0‰, $\delta^{18}O_{VSMOW}$ = 0 ‰) by analysing the GISP and SLAP2 (IAEA) international reference materials. The limit of uncertainty was ± 1.0 ‰ for $\delta^{2}H$, and ± 0.3 for $\delta^{18}O$. All samples were measured in triplicates.

Although $\delta^{13}C$ values can be used to determine the origin of alcoholic beverages, and provide evidence for the growing region and any adulteration of the product, many factors can influence the $\delta^{13}C$ value of the raw materials used for fruit distillates. These include plant maturation, age, soil and climatic region. It is for this reason that oxygen and hydrogen isotopes are used for detecting more precisely the geographic origin of a product.

Results

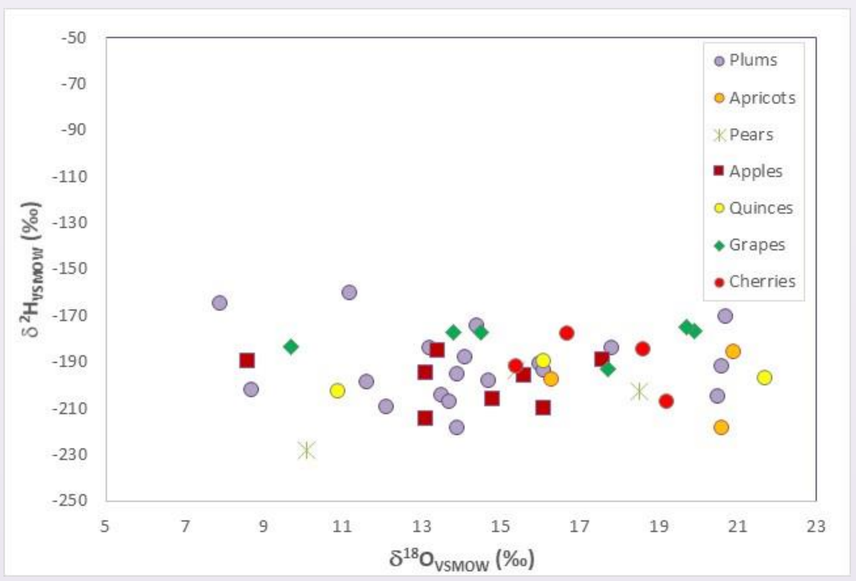


Fig.1. $\delta^{2}H$ vs. $\delta^{18}O$ plot for ethanol obtained from fruit spirits distillates

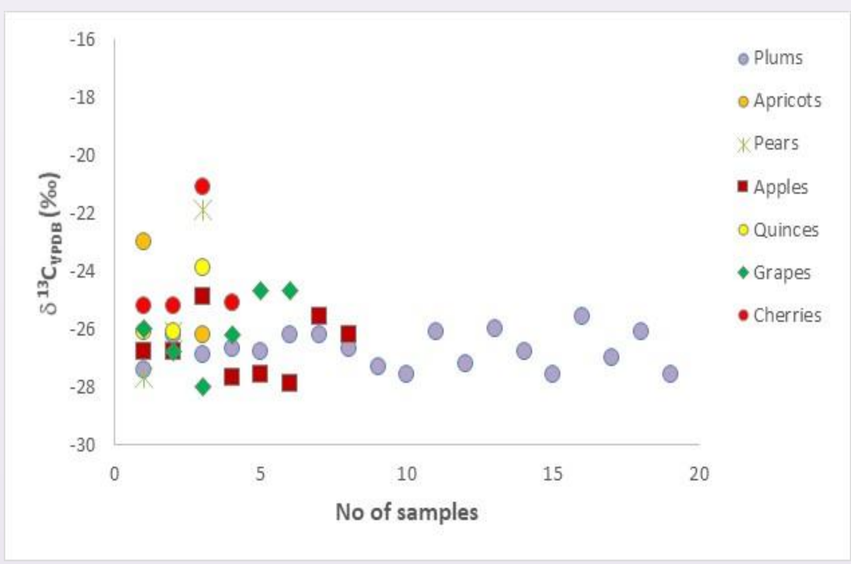
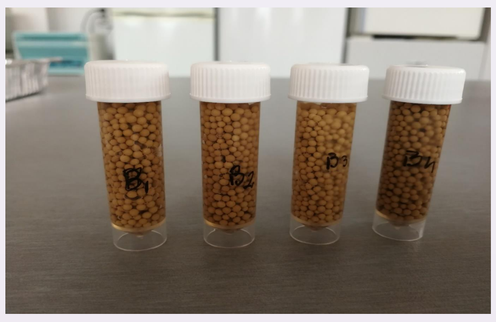


Fig.2. $\delta^{13}C$ of ethanol obtained from fruit spirits distillates



Conclusions

- the individuality of the final product is influenced by many variables during the production process, e.g: the sugar content of the fruit; the source of the water; the nature of the fuel in the drying kilns; the type of wooden cask in which it is matured; the temperature at which it is stored;
- glucose and fructose are ethanol precursors, and the fermentation process will preserve the isotopic enrichment of the leaf/fruit water. The isotopic determinations will then reflect the isotopic content of the plant water from which it originated and it will have a different isotopic content from the environmental water;
- $\delta^{2}H$ and $\delta^{18}O$ stable isotope analysis proved to be useful when tracing the origin of distilleries’ source waters and describing the various effects of initial fermentation then distillation of a substrate.

Acknowledgments.

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