Headspace gas chromatography (HSS-GC)

Major volatile compounds were analysed by gas chromatography (GC).[18] Varian 3300 gas chromatograph GC system with a split/splitless injector and a flame ionisation detector (FID) was employed. For the headspace analyses, Hewlett Packard headspace sampler HP 5890 was used. The compounds of interest were separated on a RTX-624 (30 m x 0.32 mm) (Agilent J&W, Santa Clara, CA, USA) capillary column with a film thickness of 1.8 μm with the following temperature programme: initial oven temperature was 38 °C for 4 min, then raised at 20 °C min to 170 °C, followed by 40 °C min to 190 °C and by 10 °C min to 220 °C. Operating conditions were kept constant: injector temperature: 220 °C, FID detector temperature: 250 °C, carrier gas: nitrogen, at a flow rate of 7.85 ml min^{-1}. The carrier gas pressure was 160 Psi, vial pressure 7 Psi and injection time 0.2 min. The samples were equilibrated by heating at 80°C for 10 minutes and injected by means of the headspace sampler in splitless mode (3 min). A headspace sampler was equipped with a standard 1-mL loop. The volatile compounds analysed were methanol and higher alcohols: *2*-butanol, *n*-propanol, *iso*-butanol, *n*-butanol, *iso*-amyl alcohol. Qualitative analysis was carried out by comparison of the retention times of the standards and the corresponding peak s obtained with the samples. A calibration curve for internal standardization employing pentan-3-ol as internal standard was built and used for quantification. Analyses were carried out in triplicate and their averages were calculated. Higher alcohol contents were estimated by the sum of *2*-butanol, *n*-propanol, *iso*-butanol, *n*-butanol, *iso*-amyl alcohol. Results were expressed as mg 100 mL^{-1} of absolute alcohol (AA).

HPLC analyses of polyphenol composition of wine spirits

Chemicals

Gallic, vanillic and *trans*-cinnamic acids, syringaldehyde and vanillin were purchased from Sigma-Aldrich (Steinheim, Germany). Syringic and ellagic acid were obtained also from Fluka (Buchs, Switzerland). All of them were used as standards. HPLC grade methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). The redistilled water was used in sample preparation, solutions and analyses.

Isolation of polyphenol fractions

The isolation of wine distillates polyphenol was performed by liquid–liquid extraction according to adapted method of Canas et al.[19] Extractions of samples were performed in duplicate. Samples (10 mL) were dealcoholized by means of rotary evaporator at 30 °C and

diluted to the original concentration by distilled water. Then, the sample pH was adjusted to pH = 2 with 2M HCl in order to form an aglycone and extracted three times with ethyl acetate (5 mL). The obtained three ethyl acetate extracts were combined and then evaporated to dryness in a rotary evaporator. The dry residue was dissolved in 1.5 mL of methanol and this solution was used for HPLC analyses. Extractions of samples were performed in duplicate.

Qualitative and quantitative HPLC analyses of polyphenol composition of wine spirits and brandies were performed. The analytical HPLC system was ProStar Varian equipped with a Varian Pro Star 330 photodiode array detector (Varian, Walnut Creek, CA, USA). The HPLC column was Nucleosil 5u C18 100A (Phenomenex, Torrance, CA, USA). The solvents for gradient elution were: A-0.2% o-phosphoric acid, B-methanol, C-acetonitrile. The following gradient was used: 96% A, 2% B, 2% C. The flow rate was 1.5 mL min^{-1}. Operating conditions were as follows: column temperature 30 °C and injection volume 20 µL. Chromatograms were recorded at 260, 280, 320 and 360 nm. The identification of the compounds was achieved by comparing UV spectra and the retention times of the separated peaks with the retention times of the standards. Quantification was made by the external standard method using calibration of standards as a reference and was based on peak area from HPLC analyses and mass concentration of compound. The polyphenols identified and quantified were: gallic acid (GA) and its derivate (dGA), ellagic acid (EA) and its derivate (dEA), vanillic acid (VA), syringic acid (Syr), vanillin (V), syringaldehyde (SYAL) and coniferaldehyde (CoAL). Results were expressed as mg 100 mL^{-1} of sample.

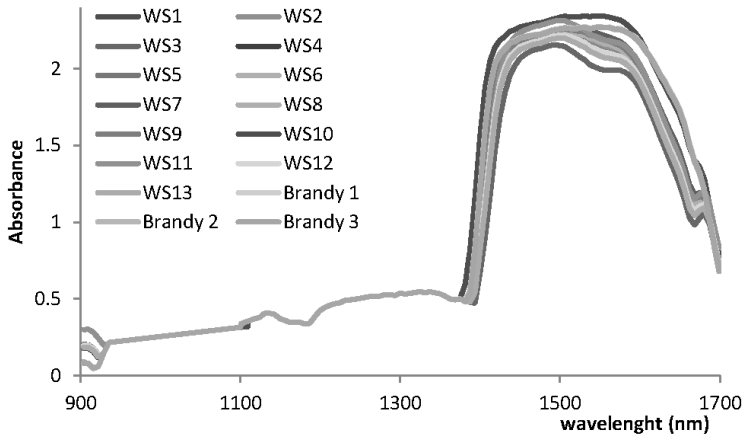

Fig S1. NIR spectra of wine spirit (WS) and brandies samples