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Short communication

Elucidation of the volatile composition of Marsala wines by using comprehensive two-dimensional gas chromatography

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ABSTRACT

The present contribution describes a research work focused on the elucidation of the composition of the headspace of Marsala wine. Four sample-types, of different ageing ("fine", "superiore secco", "superiore riserva", "vergine") were subjected to headspace solid-phase microextraction-comprehensive 2D GC analysis. At the outlet of the second GC dimension, the eluting analytes were split between a flame ionisation detector (for relative quantification purposes) and a rapid-scanning quadrupole mass spectrometer (for compound identification). Over 500 peaks were detected in each application, with a total of 128 compounds tentatively-identified considering the four sample types (mainly esters, alcohols, ketones, and aldehydes). The results attained open a door on the highly complex nature of the Marsala headspace; furthermore, they also demonstrated that the use of one-dimensional GC technologies, for the untargeted analysis of complex aroma profiles (e.g., dessert wines), is often too much of an analytical challenge.

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1. Introduction

Marsala wine, or simply "Marsala", is a well-known, highly appreciated and economically important dessert wine, produced exclusively in Sicily (Trapani province). Marsala is exported all over the world and is considered one of the four most important dessert wines together with Madeira, sherry and port. Marsala is characterised by an average alcoholic *v/v* content of 18%, and comes in three colours, namely "oro" (gold), "ambra" (amber) and "rubino" (ruby). The type of colour is dependent on the variety of grapes employed (Inzolia, Damaschino, Nerello Mascalese, etc.). Apart from colour, Marsala is classified by the degree of ageing and sugar content. Considering the former characteristic, Marsala can be: "fine" (above 1 year), "superiore" (above 2 years), "superior riserva" (above 4 years), "vergine" (above 5 years), and "stravecchio" (above 10 years). With regards to the concentration of reducing sugars, the groups are: "secco" (below 40 g/L), "semi-secco" (between 40 and 100 g/L), and "dolce" (above 100 g/L) (La Torre et al., 2008).

In general, the consumption of foods and drinks is tightly related to the stimulation of the human senses, odour and taste. Food flavour, along with texture and appearance, has a fundamental importance in the attraction of the consumer towards a particular food. With respect to odour, this sensation is generated by highly complex mixtures of volatile molecules (defined generically as aroma), in a variety of concentrations (Fisher & Scott, 1997). Currently, the analytical technique of choice for the untargeted elucidation of aroma profiles, in foods and drinks, is one-dimensional gas chromatography (1D-GC), hyphenated to a mass spectrometer (MS). It is obvious that GC–MS approaches can give qualitative (and possibly quantitative) information, but nothing on the odour sensation generated by a specific analyte. Such important information can be attained through GC-olfactometry (GC-O) (d'Acampora Zellner et al., 2008). However, one of the main problems related to the 1D-GC analysis of aromas, with either MS and/or olfactometric detection, is that such samples are excessively complex for a single GC column. The main consequence of insufficient separation power is that, often, compounds co-elute at the column outlet.

The most suitable GC technique for the untargeted analysis of highly complex samples (>200 solutes) is comprehensive 2D-GC (GC × GC), an approach introduced over twenty years ago (Liu & Phillips, 1991). GC × GC analyses are usually carried out on a

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conventional (i.e., 30 m × 0.25 mm ID) non-polar column, followed by a more polar micro-bore capillary column (i.e., 1–2 m × 0.10 mm ID). The transfer device ("modulator") operates continuously throughout the analysis and enables the trapping, and then re-injection of millisecond-wide chromatography bands. GC × GC experiments are visualised in a 2D manner, by using dedicated software. The main benefits of cryogenic GC × GC approaches, over one-dimensional GC methods, are enhanced sensitivity (peak focusing), selectivity (use of two different stationary phases), and peak capacity; an additional advantage is represented by the organised elution patterns of homologous series of compounds (i.e., linear alkanes, fatty acid methyl esters, etc.), a feature which enables reliable analyte identification, even in the absence of a mass spectrometer. For more detailed information on the technique, the reader is directed to the literature (Cortes, Winniford, Luong, & Pursch, 2009).

In general, the use of GC × GC has enabled a much deeper insight on the true composition in volatiles of real-world samples. The aroma of alcoholic beverages, in particular wine, has been often analysed by using GC × GC, using headspace solid-phase microextraction (HS-SPME), and time-of-flight MS detection (Robinson, Boss, Heymann, Solomon, & Trengove, 2011; Weldegergis, Crouch, Górecki, & de Villiers, 2011a; Weldegergis et al., 2011b; Welke, Manfroi, Zanus, Lazarotto, & Alcaraz Zini, 2012). In such studies, the complex nature of the headspace of wines was highlighted.

In the present research, an HS SPME-GC × GC-FID/MS method was developed for the analysis of Marsala. The FID trace was exploited for quantification purposes, while the MS data was used for identification. To the best of the present authors' knowledge, no GC × GC research has been performed previously on Marsala wines, and only a single paper published ("vergine" Marsala) using GC–MS (Di Stefano, 1985).

2. Experimental

2.1. Samples

Four types of Marsala, namely "fine", "superiore secco", "superiore riserva dolce", and "vergine", were kindly donated by a producer located in Marsala (Sicily, Italy). The bottles were stored at ambient temperature, in the dark, prior to analysis.

A C_7–C_{30} alkane mixture, for linear retention index (LRI) calculations, was kindly supplied by Supelco (Milan, Italy).

2.2. HS SPME process

The SPME fibres (Supelco) evaluated in the present study were: triple phase divinylbenzene (DVB)/Carboxen (CAR)/polydimethylsiloxane (PDMS) (50/30 μm), PDMS (100 μm), CAR/PDMS (75 μm). A Shimadzu AOC-5000 autosampler (Kyoto, Japan) was used for the HS-SPME operations.

Briefly, 4 mL of Marsala were introduced in a 20-mL vial. The fibre was exposed in the headspace for 30 min, at ambient laboratory temperature (25–26 °C). During the extraction the vial was agitated (clockwise-anticlockwise alternate rotation) at 500 rpm. After this process, the fibre was thermally desorbed in the GC injection port for 1.0 min at 270 °C, in splitless mode (after 1 min, a 10:1 split ratio was applied).

2.3. GC × GC-FID/MS conditions

The GC × GC–MS/FID applications were carried out on a Shimadzu GC × GC system, consisting of two independent GC2010 gas chromatographs and a QP2010 Ultra quadrupole mass spectrometer (qMS) (Kyoto, Japan). The primary GC was equipped with an AOC-20i auto-injector, a split-splitless injector (270 °C), and a cable extension for the MS connection (due to the presence of the second oven). The first column was connected by using a SGE SilTite mini-union (Ringwood, Victoria, Australia) to an uncoated tubing (1 m × 0.25 mm ID), that was passed through a heated transfer line (280 °C) into the second oven, where a dual-stage loop-type modulator (under licence from Zoex Corporation, Houston, TX) system was installed, and was finally connected to the secondary column by using a fixed outlet capillary column splitter (SGE); the latter was then linked to a 1 m × 0.10 mm ID × 0.10 μm d_f (for FID analysis) and to a 1.5 m × 0.10 mm ID × 0.10 μm d_f column (for MS analysis). In both cases, a Supelcowax-10 (100% polyethylene glycol) stationary phase was employed (Supelco). Cryogenic modulation was applied every 5 s, with a hot jet (340 °C) duration of 375 ms. The first column was an SLB-5 ms 30 m × 0.25 mm ID × 0.25 μm d_f column (silphenylene polymer virtually equivalent in polarity to poly (5% diphenyl/95% methylsiloxane); Supelco). Carrier (He) pressure: 150 kPa (constant linear velocity). Temperature program (equivalent in both ovens): from 50 °C (1 min) to 280 °C, at 3 °C/min.

MS parameters: the sample was analysed in full scan mode, with a scan speed of 10,000 amu/s, a mass range of m/z 40–360, and a sampling frequency of 25 spectra/s; interface and ion source temperatures were 250 and 200 °C, respectively. MS ionisation mode was electron impact ionisation. Data were acquired by using the GCMSsolution software ver. 4.0, while the MS database was the FFNSC 2.0 (Shimadzu). Bidimensional chromatograms were generated by using the ChromSquare software ver. 1.6 (Shimadzu Europe, Duisberg, Germany).

FID parameters: temperature was 280 °C; acquisition frequency: 125 Hz; gases: make-up (He): 40 mL/min; H_2: 40 mL/min; air: 400 mL/min.

3. Results and discussion

3.1. SPME method optimisation

Initially, the SPME operation conditions were optimised considering fibre stationary phase, extraction time, and desorption time. The three extraction phases were evaluated at two times (15 and 45 min), and using a fibre desorption time of 5 min (270 °C). With regards to the extraction temperature, no additional heating was used because the objective of the research was to provide a profile of Marsala volatiles, which is best performed at ambient temperature. Heating could potentially accelerate the extraction period, but would also alter the "normal" composition of Marsala headspace (Marsala is consumed at ambient temperature), and, consequently, the HS SPME-GC × GC fingerprint would not faithfully represent that of the Marsala volatile composition.

With regards to the fibre selectivity, the heterogenous composition (in terms of polarity) of Marsala headspace must be considered. In fact, Marsala volatiles range from acids, to alcohols, onto esters, aldehydes and ketones, down to hydrocarbons. The PDMS liquid polymer showed a poor coverage for the more polar volatiles (i.e., alcohols, acids, aldehydes); on the other hand, the mixed DVB/CAR/PDMS and CAR/PDMS fibres, which consist of a porous solid and liquid polymer, did not discriminate between low and high-polarity volatiles. However, because CAR (particle size: 2–10 μm) is characterised by smaller pores with respect to DVB, the CAR/PDMS fibre gave an excellent performance towards the lower MW volatiles, and was much less selective towards the higher MW ones (>200 amu). Overall, it was the DVB/CAR/PDMS phase that provided the best coverage in terms of polarity and analyte MW.

After defining the most appropriate fibre, four different extraction periods were evaluated, namely 15, 30, 45, 60 and 75 min. It

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