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Analytical Methods

Determination of sotolon content in South African white wines by two novel HPLC–UV and UPLC–MS methods

Mario Gabrielli [a], Astrid Buica [b], Daniela Fracassetti [a], Marietjie Stander [c,d], Antonio Tirelli [a], Wessel J. du Toit [b,*]

[a] Department of Food, Environmental and Nutritional Sciences, Università degli Studi di Milano, Via G. Celoria 2, 20133 Milano, Italy
[b] Department of Viticulture and Oenology, University of Stellenbosch, Private Bag X1, Matieland (Stellenbosch) 7602, South Africa
[c] Central Analytical Facility (CAF), University of Stellenbosch, Private Bag X1, Matieland (Stellenbosch) 7602, South Africa
[d] Department of Biochemistry, University of Stellenbosch, Private Bag X1, Matieland (Stellenbosch) 7602, South Africa

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ABSTRACT

Sotolon has been reported to play an important role in the atypical ageing and aroma character of many wines. A number of analytical techniques for sotolon analysis in wine have been reported, but these often require extensive sample preparation. In this work we report a HPLC–UV method and a novel UPLC–MS method to determine sotolon concentrations in white wines with little sample preparation applied for the first time for the evaluation of sotolon levels in South African wines. The validation showed that the instrumental methods had good accuracy, repeatability and linearity, but the UPLC–MS method proved more sensitive. For both methods, quantification limits were lower than the sotolon odour threshold in wine (10 μg/L), 0.86 μg/L and 0.013 μg/L, for HPLC–UV and UPLC–MS methods, respectively. Sotolon levels in 65 South African white wines were often found to be lower than the reported odour threshold, with the highest concentration being 9.11 μg/L. However, for low levels (<1 μg/L), unknown interferences in certain wines led to sotolon not being quantified with the HPLC–UV method, which made the UPLC–MS method more suitable.

1. Introduction

Sotolon (3-hydroxy-4,5-dimethyl-2(5)-furanone) is a powerful flavour compound with an intense spicy/curry odour (Girardon, Sauvaire, Baccou, & Bessiere, 1986). Sotolon has an aroma associated with aged sake (Takahashi, Tadenuma, & Sato, 1976), roasted coffee (Blank, Sen, & Grosh, 1992), fenugreek (Girardon et al., 1986) and sugar cane (Tokitomo, Kobayashi, Yamanishi, & Murahi, 1980). Sotolon has been identified and quantified in different wines, such as botrytised (or noble rot) wines (5–20 μg/L) (Masuda, Okawa, Nishimura, & Yunome, 1984), port (5–958 μg/L) (Silva Ferreira, Barbe, & Bertrand, 2003), vin Javen (120–268 μg/L) (Pham, Guichard, Schlich, & Charpentier, 1995), sherry (0–500 μg/L) (Martin, Etiévant, Le Quéré, & Schlich, 1992) and Madeira (0–2 000 μg/L) (Camara, Marques, Alves, & Silva Ferreira, 2004), and in barrel-aged white wines (0–140 μg/L) (Lavigne, Pons, Darriet, & Dubourdieu, 2008). Its odour threshold is extremely low: 0.02 μg/L in air (Blank, Lin, Fumeaux, Welti, & Fay, 1996), 0.3 μg/L in water (nasal detection) (Blank et al., 1996) and 10 μg/L in white wine (human perception) (Guichard, Pham, & Etiévant, 1993). Although it is associated to a typical flavour note in Madeira, port, sherry and long-aged sweet wines, sotolon is considered to be one of the compounds responsible for the atypical ageing and oxidative off-flavour in dry white wines when its concentration is higher than the odour threshold (Du Toit, Marais, Pretorius, & Du Toit, 2006).

Several pathways for the formation of sotolon are reported in the literature. It can be produced by thermal degradation of intermediate compounds of the Maillard reaction (Blank et al., 1996; Guerra & Yaylayan, 2011; Hofmann & Schieberle, 1997). Cutzach, Chatonnet, and Dubourdieu (1999) showed a pathway for the formation of sotolon via aldol condensation between α-keto butyric acid and acetaldehyde. Konig et al. (1999) explained that sotolon is produced by the reaction between ethanol and ascorbic acid. During winemaking and ageing, sotolon formation is affected by chemical and physical factors such as the presence of oxygen (Cutzach et al., 1999; Lavigne et al., 2008), the reducing sugar concentration (Camara et al., 2004), storage temperature and time

* Corresponding author.
E-mail address: wdutoit@sun.ac.za (W.J. du Toit).

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(Cutzach et al., 1999), and concentrations of certain antioxidants (e.g. sulphur dioxide, glutathione) (Dubourdieu & Lavigne, 2004).

Due to the number of physical and chemical factors affecting the formation of sotolon in wine, this compound was suggested as a chemical marker of the shelf-life for dry white wine (Lavigne & Dubourdieu, 2004). However, the levels of sotolon in South African white wine have not been investigated before.

Several analytical techniques have been reported for the determination of sotolon in wine, including Multi-Dimensional Gas Chromatography (MDGC–MS) and High-Resolution GC (HRGC–MS) (Konig et al., 1999); High-Resolution GC Olfactometry (HRGC–MS–O) (Escudero, Cacho, & Ferreira, 2000); GC Olfactometry (GC–O) (Silva Ferreira et al., 2003); Two Dimensional Capillary GC (2D-CGC) (Dugo et al., 2014; Martin & Etiévant, 1991); GC–MS (Castro, Martins, Teixeira, & Silva Ferreira, 2014; Pons, Lavigne, Landais, Darriet, & Dubourdieu, 2010; Zea, Moyano, Ruiz, & Medina, 2013); Two Dimensional GC (2D-GC) (Martin et al., 1992); and High Pressure Liquid Chromatography (HPLC–UV) (Guichard et al., 1993). Moreover, the sotolon concentration in wine is usually low and the compound has high boiling temperature (184 °C), both affecting negatively the sensitivity of the analytical methods based on head space sampling technique (DHS and SPME) (Ferreira, Jarauta, López, & Cacho, 2003; Ferreira, Ortega, Escudero, & Cacho, 2000). The sample preparation requires both an extraction step (liquid/liquid extraction or solid phase extraction (SPE)) followed by a concentration step prior the chromatographic separation (Cutzach et al., 1999; Konig et al., 1999). Generally, these reported methods use either instrumentation that is not standard in oenology laboratories or long extraction time (Escudero et al., 2000), and substantial volumes of both sample and solvents (Konig et al., 1999; Schneider, Baumes, Bayonove, & Razungles, 1998; Takahashi et al., 1976).

The two main aims of this study thus were to develop, validate and compare two fast and reproducible chromatographic methods (UPLC–MS and HPLC–UV) for sotolon analysis in wine, and to use these methods to assess sotolon levels in South African white wines in order to understand the occurrence of atypical ageing causing a decrease of wine shelf-life.

2. Materials and methods

2.1. Chemicals

4,5-Dimethyl-3-hydroxy-2,5-dihydrofuran-2-one (⩾97%), dichloromethane (⩾99.8%), sodium chloride (⩾99.5%), methanol (⩾99.9%), acetonitrile LC–MS CHROMASOLV® (⩾99.0%), isopropanol LC–MS CHROMASOLV® (⩾99.0%) and anhydrous sodium sulphate (⩾99.0%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). UPLC water was obtained from a Milli-Q filtration system (Millipore Filter Cor., Bedford, MA, USA). Polyvinylpolypyrrolidone (PVPP) resin was purchased from Dal Cin Gildo spa (Sesto San Giovanni, Milano, Italy). The model wine contained 12% (v/v) ethanol and 5 g/L of tartaric acid, and the pH was adjusted to 3.5 with sodium hydroxide (Sigma–Aldrich St. Louis, MO, USA).

2.2. White wine samples

Sotolon analysis was carried out on 70 commercial South African white wines. The commercial wines were produced from ten different grape cultivars (Sauvignon blanc, Chardonnay, Chenin blanc, Viognier, Semillon, Grenache blanc, Pinot Grigio, Colombard, Gewurztraminer and Rhine Riesling) and sixteen different vintages (from 1983 to 2013). The wine samples coded by number (1–65) were sourced directly from local cellars, while the wines coded by letter (a–e) were stored for 2 years at 37 °C.

2.3. Sample preparation

The sample preparation was done according to Gabrielli (2014), Gabrielli, Fracassetti, and Tirelli (2014). The equivalent of 3 g/L NaCl was added to 30 mL of white wine. The wine was extracted twice with 20 mL dichloromethane for 10 min with stirring. The organic phases were combined and 2 g anhydrous Na_2SO_4 was added to remove traces of water. Dichloromethane was evaporated to dryness under a gentle nitrogen stream, and the dry material was re-dissolved in 2 mL of 5% methanol solution. The concentrated extract was further purified with 50 mg of PVPP resin by dispersion in the sample. The solution was filtered (0.22 μm PVDF, Millipore, MO, USA) before injection.

2.4. UPLC–MS/MS and HPLC–UV analysis

UPLC–MS separations were performed with a Waters Acquity H Class UPLC system connected to a Waters Xevo triple quadrupole mass spectrometer (Waters, Milford, MA, USA). The column used was a BEH C18, 2.1 × 100 mm, 1.7 μm (Waters, Milford, MA, USA). Data were acquired in multiple reaction monitoring (MRM) mode, electrospray positive ionisation, precursor ion at m/z 129, and the product ions at m/z 55 and 83, using a collision energy of 20 V and 15 V, respectively. A cone voltage of 20 V was used. The desolvation temperature was set at 400 °C, and the desolvation gas was 900 L/h. A capillary voltage of 3.5 kV was used and the rest of the MS settings were optimised for best sensitivity. The mobile phases were (A) 1% formic acid in water and (B) methanol:acetonitrile:iso-propanol (49:49:2), and the flow rate was 0.4 mL/min. The injection volume was 3 μL and the column temperature was at 30 °C.

HPLC–UV separations were performed with an Agilent 1260 Series system fitted with a diode array detector (Agilent, Palo Alto, CA, USA). The column used was a Kinetex C18 100 × 3 mm × 2.6 μm, from Phenomenex (Torrence, CA, USA). The sotolon was detected and quantified at 235 nm. The mobile phases used were (A) water and (B) methanol, and the flow rate was 0.45 mL/min. The injection volume was 20 μL and the column temperature was 30 °C. The gradients are reported in Table 1.

Table 1
Gradients: UPLC–MS (A: formic acid 1% and B: methanol:acetonitrile:iso-propanol (49:49:2)) and HPLC–UV (A: water and B: methanol).

ULPC–MS gradient				HPLC–UV gradient			
Time (min.)	Flow (mL/min)	Eluent A (%)	Eluent B (%)	Time (min.)	Flow (mL/min)	Eluent A (%)	Eluent B (%)
0.0	0.4	91	9	0	0.45	95	5
3.0	0.4	91	9	8	0.45	95	5
3.1	0.4	30	70	9	0.45	0	100
4.0	0.4	0	100	11	0.45	0	100
5.0	0.4	0	100	12	0.45	95	5
5.1	0.4	91	9	20	0.45	95	5
6.5	0.4	91	9				