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Short communication

Quantification of megastigmatrienone, a potential contributor to tobacco aroma in spirits

Davide Slaghenaufi *, Marie-Claire Perello, Stéphanie Marchand, Gilles de Revel

Univ. Bordeaux, ISVV, EA 4577, Unité de Recherche Œnologie, 33882 Villenave d'Ornon, France
INRA, ISVV, USC 1366 Œnologie, 33882 Villenave d'Ornon, France

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ABSTRACT

A SPME–GC–MS method was adapted and validated in order to quantify 5 megastigmatrienones and related odorous compounds from oak wood: guaiacol, *cis*-whisky lactone, *trans*-whisky lactone, γ-nonalactone, eugenol, vanillin, and acetovanillone in a single run. The five megastigmatrienone isomers (tabanones) were quantified, for the first time, in Cognac, Armagnac and rum, as contributors to tobacco-like aromas. Spirits aged in oak barrels contain higher amounts, but megastigmatrienones are also present in freshly-distilled spirits. Statistical analysis revealed that freshly-distilled and barrel-aged spirits were differentiated by their megastigma-4,7*E*,9-trien-3-one levels. The Armagnac and Cognac samples were distinguished by their concentrations of the megastigma-4,6*Z*,8*E*-trien-3-one isomer.

1. Introduction

Over 500 aroma compounds have been detected in Cognac (Cantagrel, 2003), mainly esters, alcohols, aldehydes, and volatile acids. Spirits aged in oak barrels are characterized by woody aromas, like vanilla, cloves, and coconut. The volatile compounds mainly responsible for these notes are vanillin, eugenol, and whisky lactone, respectively. However other descriptors are associated with old brandies and whiskies, including tobacco, cigar box, and incense. Megastigmatrienone, otherwise known as "tabanone", was hypothesized to be the volatile compound responsible for this aroma, as it is a key compound in Burley tobacco flavor (Aasen, Kimland, Almquist, & Enzell, 1972; Lloyd et al., 1976; Ohloff, 1978). Five isomers of megastigmatrienone : megastigma-4,6*Z*,8*E*-trien-3-one (MEG 1), megastigma-4,7*E*,9-trien-3-one (MEG 2), megastigma-4,6*E*,8*E*-trien-3-one (MEG 3), megastigma-4,6*E*,8*Z*-trien-3-one (MEG 4), and megastigma-4,6*Z*,8*Z*-trien-3-one (MEG 5) (Fig. 1) were recently quantified in wines (Slaghenaufi, Perello, Marchand-Marion, & de Revel, 2014) and found to contribute to tobacco-like aromas (Arbulu et al., 2013). The odor detection threshold of a mixture of the five isomers has been evaluated at 8 μg/L in water (Slaghenaufi, 2012), but each isomer contributes specific notes to the overall aroma (Slaghenaufi et al., 2014).

To date, little is known about the origin of megastigmatrienone. First results indicate that is probably produced by carotenoid degradation throughout wine aging (Slaghenaufi et al., 2014).

Carotenoid degradation leads to the formation of 3-oxo-α-ionol, which may produce megastigmatrienone under acidic conditions. The presence of megastigmatrienone in grapes has yet to be investigated.

Wine aged in oak barrels generally has a higher megastigmatrienone content and it has also been identified as a free volatile compound in oak wood (Sefton, Francis, & Williams, 1990). A megastigmatrienone precursor was recently identified in oak wood: macarangioside E (Slaghenaufi et al., 2013). It has been shown (Slaghenaufi et al., 2013) that this compound is degraded at high temperatures to form megastigmatrienone, 3-oxo-α-ionol, and ketoisophorone, so spirits may be further enriched with these compounds by aging in toasted oak-wood barrels. The contribution of oak barrels to total megastigmatrienone content may be greater in spirits than wine, due to the higher alcohol content (more effective solvent) and the longer contact time with wood (Spillman, Iland, & Sefton, 1998).

The aim of this work was to detect and quantify the five megastigmatrienone isomers in spirits. The SPME–GC–MS method developed previously (Carrillo, Garrido-López, & Tena, 2006) was improved to handle a high ethanol content matrix, like spirits. In

* Corresponding author at: Univ. Bordeaux, ISVV, EA 4577, Unité de Recherche Œnologie, 33882 Villenave d'Ornon, France.
E-mail address: davideslaghenaufi@gmail.com (D. Slaghenaufi).

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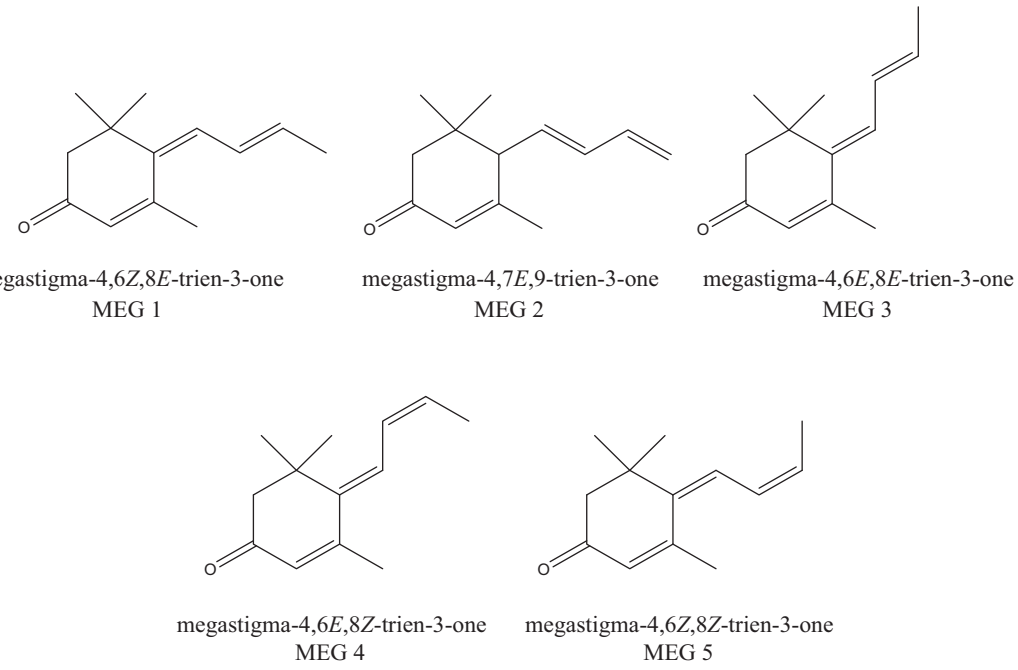

Fig. 1. Structure of the five megastigmatrienone isomers.

fact a high level of ethanol in samples can limit the adsorption of compounds onto the SPME fiber (Castro, Natera Marín, García Moreno, & García Barroso, 2003). The modifications made it possible to quantify megastigmatrienone and oak volatile compounds in a single run.

A second goal, thanks to the improved method, was to establish the role played by wood on megastigmatrienone content during spirits storage in barrels.

2. Material and methods

2.1. Samples

Spirits samples were taken from 63 Armagnacs, 32 Cognacs, and 13 rums, giving a total of 108 spirits (between 40% and 70% alcohol). Armagnac samples consisting of both finished commercial spirits and freshly-distilled spirits intended for Armagnac production were kindly provided by several distilleries. Cognac and rum samples were taken from commercial products from several different brands.

2.2. Reagents

Megastigmatrienone was kindly provided by Symrise AG (Holzminden Germany) as a mix of isomers (m/m): 11% MEG 1, 32% MEG 2, 35% MEG 3, 4% MEG 4, and 18% MEG 5. Dodecan-1-ol at 98% purity (CAS: 112-53-8), used as an internal standard, was supplied by (Acros organic). Milli-Q quality water (18.2 MΩ cm^{-1}) was produced from distilled water by a Milli-Q Plus water system (Millipore, Saint-Quentin-en-Yvelines, France). Guaiacol (CAS: 90-05-1; purity 99%), γ-nonalactone (CAS: 104-61-0; purity 97%), eugenol (CAS: 97-53-0; purity 98%), and both whisky-lactones (CAS: 39212-23-2; purity 98%; mixture of isomers) were purchased from Sigma-Aldrich Chemicals (St Quentin Fallavier, France), and acetovanillone (CAS: 498-02-2; purity 98%) and vanillin (CAS: 148-53-8; purity 99%) from Prolabo (Fontenay-sous-bois, France). Sodium chloride (CAS: 7647-14-5; purity 99%) was supplied by VWR-Prolabo (Fontenay-sous-bois, France).

2.3. Sample preparation

Samples were diluted 10-fold in MQ water. Ten mL samples were collected and placed in 20 mL vials containing 3.5 g sodium chloride, spiked with 10 μL internal standard (dodecan-1-ol at 9 mg/L in ethanol), and the vial was sealed with a PTFE-lined cap (Chromoptic, France).

2.4. HS-SPME extraction

Volatiles were extracted by exposing a divinylbenzene–carboxen–polydimethylsiloxane 50/30 μm (DVB/CAR/PDMS) fiber in the sample head space. The fiber was conditioned as recommended by the manufacturer prior to use. Headspace SPME was performed with the following parameters: incubation/extraction temperature: 70 °C; incubation time: 2 min; extraction time: 60 min; agitation rate: 500 rpm. Desorption was performed in the injector at 250 °C for 300 s. The method was adapted from Slaghenaufi et al., 2014.

2.5. Analysis conditions

GC–MS analysis was carried out on an HP 5890 gas chromatograph system coupled to an HP 5972 quadrupole mass spectrometer (Agilent), equipped with a Gerstel MPS2 autosampler (Müllheim/Ruhr, Germany), using injection in splitless mode. Separation was performed on a BP-21 capillary column (50 m × 0.32 mm, 0.25 μm film thicknesses, SGE, Courtaboeuf, France). The carrier gas was helium N55 with a column-head pressure of 8 psi during the entire chromatographic run. The oven temperature was programmed at 40 °C for 2 min, then raised to 220 °C at 3 °C/min, and held at 220 °C for 20 min. Detection was in selected ion monitoring (SIM) mode with the electron ionization (70 eV) source at 250 °C. The ions were monitored as reported in the literature (Carrillo et al., 2006; Slaghenaufi et al., 2014) (Table 1).