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Investigation and Sensory Characterization of 1,4-Cineole: A Potential Aromatic Marker of Australian Cabernet Sauvignon Wine

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Supporting Information

ABSTRACT: This work reports the quantitation and sensory characterization of 1,4-cineole in red wine for the first time. A headspace−solid-phase microextraction−gas chromatography−mass spectrometry (HS−SPME−GC−MS) method was developed to quantitate 1,4-cineole and 1,8-cineole in 104 commercial Australian red wines. 1,4-Cineole was detected in all of the wines analyzed, with concentrations ranging from 0.023 to 1.6 μg/L. An important varietal effect was observed, with concentrations of 1,4-cineole in Cabernet Sauvignon wines (mean of 0.6 ± 0.3 μg/L) significantly higher than in Shiraz (0.07 ± 0.04 μg/L) and Pinot Noir (0.2 ± 0.2 μg/L) wines. Regional variations of both cineole isomer concentrations have been measured between wines originating from different Australian regions. Sensory studies demonstrated that the addition of 0.54 μg/L 1,4-cineole in a Cabernet Sauvignon wine, to produce a final concentration of 0.63 μg/L, was perceived significantly by a sensory panel ($p < 0.05$). Descriptive analyses revealed that 1,4-cineole and 1,8-cineole may contribute to the hay, dried herbs, and blackcurrant aromas reported in Australian Cabernet Sauvignon wines and may be potential markers of regional typicality of these wines.

KEYWORDS: *monoterpenes, typicality, aromatic herbs, red wines*

INTRODUCTION

Originating from Bordeaux, France, Cabernet Sauvignon, a cross between Cabernet Franc and Sauvignon Blanc, is the most planted grape variety in the world.[1] The success could be explained by the very fine wines that this cultivar can produce, leading to the production of numerous iconic wines all around the world. In Australia, Cabernet Sauvignon is the second most abundant red cultivar after Shiraz and is used for the production of varietal wines and red blends that encompass a wide range of quality and styles.

The aromatic spectrum of Cabernet Sauvignon wines is highly dependent upon the wine origin and can exhibit aromas as diverse as "blackcurrant", "cassis", "leaves", "green pepper", "mint", "cedar", "spice", and "smoke".[2−5] Australian Cabernet Sauvignon wines aromas are often described using specific attributes, such as "eucalyptus", "mint", "dry leaves", and "dried herbs",[4,6] that differ from the common description of Bordeaux Cabernet Sauvignon wines, often used as reference for this cultivar.[3] Eucalyptus aroma is often reported in red wines coming from regions known to have eucalyptus trees in the vicinity of the vineyard.[7−9] It was shown that 1,8-cineole (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane, also known as eucalyptol) (Figure 1), a major constituent of eucalyptus essential oil, played an important role in the occurrence of "eucalyptus" character in red wine.[7] In parallel, other studies suggest that

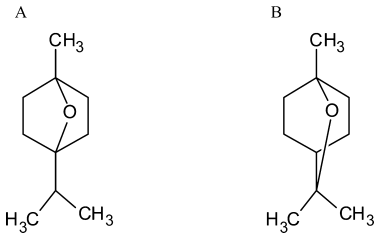

Figure 1. Chemical structure of (A) 1,4-cineole and (B) 1,8-cineole.

1,8-cineole found in Australian wines could also be derived from grapes, particularly in Cabernet Sauvignon.[10,11]

1,4-Cineole (4-methyl-1-propan-2-yl-7-oxabicyclo[2.2.1]-heptane) (Figure 1), another monoterpene with a similar structure and natural occurrence[12−14] to that of 1,8-cineole, has also been reported in red wines.[15,16] However, to our knowledge, 1,4-cineole has never been quantified in wines, and while 1,8-cineole has been subjected to wide sensory investigations as a result of the extensive research on eucalyptus essential oil composition,[17] the sensory information on 1,4-cineole is limited. The aroma of 1,4-cineole has been described

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Table 1. Validation Parameters of the Method Developed To Quantitate 1,4-Cineole and 1,8-Cineole in Red Wines

compound	RI[a] DB-wax/HP-5	quant. ion (m/z)[b]	linearity range (μg/L)	mean r^2 [c] (n = 3)	slope reproducibility (%) (n = 3)	LOD[d] (μg/L)	LOQ[d] (μg/L)	repeatability (%) (n = 10) low[e]	repeatability (%) (n = 10) medium[e]	reproducibility (%) (n = 5)	average recovery (%) (n = 3)
1,4-cineole	1185/1014	111	0.025−2.5	0.9993 ± 0.0007	1.7	0.001	0.004	6.3	4.4	4.7	98 ± 9
1,8-cineole	1210/1030	108	0.1−10	0.9997 ± 0.0002	4.5	0.003	0.01	3.7	3.9	2.9	93 ± 2

[a]RI for Kovats retention index on polar (DB-Wax) and apolar (HP-5) columns. [b]Quant. ion = ions used for quantitation. [c]r^2 = coefficient of determination. [d]The limits of detection (LODs) (concentration for signal/noise = 3) and the limits of quantitation (LOQs) (concentration for signal/noise = 10) were manually calculated from the ratio of the peak heights to the average noise before and after each peak. [e]Repeatability was assessed for low concentrations at 0.05 and 0.4 μg/L for 1,4-cineole and 1,8-cineole, respectively, and for medium concentrations at 0.5 and 2 μg/L, respectively.

as "minty", "cooling piney", "camphoraceous", and "eucalyptol-like",[18] but no detection threshold of this compound has been reported in the literature.

Because of the comparable natural occurrence of 1,4-cineole and 1,8-cineole, their olfactory similarity, and the importance of 1,8-cineole in Australian red wines, this study aimed to investigate the occurrence and potential contribution of 1,4-cineole to red wine aroma. A headspace−solid-phase microextraction−gas chromatography−mass spectrometry (HS−SPME−GC−MS) method was developed and validated to quantitate 1,4-cineole and 1,8-cineole in Australian red wines. Discriminative and descriptive sensory methods were used to characterize the contribution of 1,4-cineole, both independently and in combination with 1,8-cineole, upon Cabernet Sauvignon wine aroma.

MATERIALS AND METHODS

Material. Standards including 1,4-cineole (98.5%), 1,8-cineole (99%), octan-2-ol (97%), 3-isobutyl-2-methoxypyrazine (IBMP, 99%), and menthol (99%) were purchased from Sigma-Aldrich (Castle Hill, New South Wales, Australia). Stock and working solutions of standards were prepared volumetrically in ethanol (AnalaR NORMAPUR, VWR, Fontenay-sous-Bois, France) and stored at −20 °C. Water was obtained from a Milli-Q purification system (Millipore, North Ryde, New South Wales, Australia). Sodium chloride (NaCl) was purchased from Merck (Darmstadt, Germany). Deionized water was obtained from a Milli-Q mixed bed resin system (18 MΩ/cm and 25 °C).

Wines. A range of commercial Australian red wines (104 in total) comprising of 51 Cabernet Sauvignon, 4 Cabernet Sauvignon/Merlot blends (60−80% Cabernet Sauvignon), 27 Shiraz, and 22 Pinot Noir wines were purchased. The wines originated from important regions for Cabernet Sauvignon, Shiraz, and Pinot Noir wine production. Cabernet Sauvignon wines (varietal and blends) were from Coonawarra (31%), Margaret River (27%), Barossa and McLaren Vale (25%), and other regions located in South Australia, Victoria, and New South Wales (17%). Shiraz wines were from Barossa and McLaren Vale (37%), Coonawarra (19%), Margaret River (11%), and other regions located in South Australia, Victoria, and New South Wales (33%). Pinot Noir wines were from Victoria (50%), Orange (36%), other regions located in South Australia and Tasmania (14%). Cabernet Sauvignon and Shiraz wines were mainly from 2012, 2011, 2010, and 2009 (mean age of 3.5 years). Pinot Noir wines were from 2013, 2012, and 2011 (mean age of 2 years).

Cineole Isomer Analysis. The method for quantitating 1,4-cineole and 1,8-cineole by HS−SPME−GC−MS was developed in combination of previously published methods for wine volatiles.[8,19]

Spiking and Sample Preparation. The development and the validation of the method were carried out using Australian red wines from the 2013 vintage. The method consisted of adding 20 μL of a stock solution of octan-2-ol (internal standard) at 5 mg/L in absolute ethanol to 10 mL of wine. To a 20 mL headspace vial 3 g of NaCl, 5 mL of wine spiked with internal standard, and 5 mL of deionized water were added. The vial was then tightly sealed with a polytetrafluoroethylene (PTFE)-lined cap, and contents were homogenized.

Instrumentation. An Agilent 7890A gas chromatograph, equipped with a Gerstel multipurpose sampler with automated SPME capability, interfaced to an Agilent 5975C triple-axis mass detector was used. A MSD Chemstation E.02.00.493 (Agilent Technologies, Ltd.) and National Institute of Standards and Technology (NIST) MS Search 2.0 version 2008 were used to control the instrument and for mass spectra assessment. Prepared samples were placed in the tray until analysis, whereupon vials were transferred to a heater block. The extraction consisted of preincubating the vial for 10 min at 40 °C with swirling at 500 rpm, inserting a 1 cm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 μm fiber (Supelco, Bellefonte, PA) into the headspace for 30 min at 40 °C while the solution was swirled again. The fiber was then transferred to the injector for desorption at 250 °C for 1 min, withdrawn, and injected into a second injector set at 270 °C with a 50:1 split for 10 min with a 10 mL/min purge flow to clean the fiber, prior to the next sample analysis. A fused silica capillary column (DB-Waxetr, 60 m × 0.25 mm inner diameter, 0.25 μm film thickness, Agilent Technologies, Santa Clara, CA) was used for compound separation by gas chromatography. The injector block was fitted with a 1 mm internal diameter borosilicate liner (SGE), and the injector temperature set to 260 °C in splitless mode. The oven temperature program commenced at 40 °C for 5 min, increased to 120 °C at a rate of 3 °C/min, with a final increase to 220 °C at a rate of 15 °C/min, and held for 15 min. The total run time was 53.3 min. The flow rate of ultrahigh-purity helium gas was constant at 3 mL/min. The MS source, quadrupole, and transfer line temperatures were set to 230, 150, and 275 °C, respectively.

Compound Identification and Quantitative Analysis. The identification of 1,4-cineole and 1,8-cineole (Figure 1) in wines was performed by comparing retention times and mass spectra (scan mode) to those of pure standards at 20 μg/L in water and red wine. Kovats retention indices (RIs) were checked for each compound using a commercial mixture of n-alkanes (Sigma, Steinheim, Germany), with an identical oven ramp profile and gas flow rates as used for the final analyzes on DB-Waxetr (60 m × 0.25 mm inner diameter, 0.25 μm film thickness) and HP-5MS (30 m × 0.25 mm inner diameter, 0.25 μm film thickness) columns. Mass spectral data were collected in both selective ion monitoring (SIM) and scan mode (m/z 35−350) at an ionization voltage of 70 eV. The mass spectra of both cineole isomers are available in the NIST 08 MS database. Quantifier and qualifier ions were selected as described in the literature for 1,8-cineole[8] and based on the best signal/noise ratio measured in red wines for 1,4-cineole. The ions monitored in SIM runs were m/z 71, 81, 93, 108, 111, 125, 139, and 154 for the cineole isomers and m/z 45 and 55 for octan-2-ol. The quantitation ions used for the cineole isomers are listed in Table 1, while m/z 45 was used for octan-2-ol. The other ions were used as qualifiers.

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Table 2. Code of Samples Used for Sensory Analysis

code	description	concentration
wat	water	
CS	Cabernet Sauvignon wine	3.4 ng/L IBMP
		0.09 μg/L 1,4-cineole
CSi	CS wine spiked with IBMP	10 ng/L IBMP
wat + 1,4c-0.13	1,4-cineole in water	0.13 μg/L 1,4-cineole
wat + 1,4c-0.27	1,4-cineole in water	0.27 μg/L 1,4-cineole
CS + 1,4c-0.13	1,4-cineole in CS wine	0.22 μg/L 1,4-cineole
CS + 1,4c-0.27	1,4-cineole in CS wine	0.36 μg/L 1,4-cineole
CS + 1,4c-0.54	1,4-cineole in CS wine	0.63 μg/L 1,4-cineole
CS + 1,8c	1,8-cineole in CS wine	2.5 μg/L 1,8-cineole
CSi + 1,4c	1,4-cineole in CSi wine	1.6 μg/L 1,4-cineole
CSi + 1,8c	1,8-cineole in CSi wine	2.5 μg/L 1,8-cineole
CSi + 1,8c-10	1,8-cineole in CSi wine	10 μg/L 1,8-cineole
CSi + 1,4c + 1,8c	1,4-cineole + 1,8-cineole in CSi wine	1.6 μg/L 1,4-cineole
		2.5 μg/L 1,8-cineole
CSi + 1,4c + 1,8c-10	1,4-cineole + 1,8-cineole in CSi wine	1.6 μg/L 1,4-cineole
		10 μg/L 1,8-cineole

Method Validation. Linearity was validated by a series of seven standard additions of 1,4-cineole and 1,8-cineole in three different commercial red wines (Shiraz, Cabernet Sauvignon, and Merlot). The initial concentrations of 1,4-cineole and 1,8-cineole in the wines used for validation were below 0.1 and 0.5 μg/L, respectively. The calibration ranges are displayed in Table 1. The precision of the method was assessed by analyzing 10 replicates of a commercial Shiraz with 1,4-cineole and 1,8-cineole at 0.05 and 0.4 μg/L, respectively, which covered the low range of concentrations. A second trial for the assessment of precision was made at a medium range of the concentration for both 1,4-cineole and 1,8-cineole, with the same wine spiked at 0.5 and 2 μg/L, respectively. The robustness of the method was determined by analyzing five replicates of the same spiked wine over a period of 2 weeks. For the accuracy study (recovery), three different varietal red wines (Cabernet Sauvignon, Shiraz, and Pinot Noir) were spiked with 1,4-cineole and 1,8-cineole at the same concentrations as used for repeatability. To ensure that the accuracy of the method was maintained, a control red wine sample spiked with cineole isomers as previously indicated was regularly included in the set of samples to be quantitated.

Sensory Analyses. *General Conditions.* Sensory analyses were performed with samples prepared in water and wine as previously described.[20] Sample assessments were undertaken in a temperature-controlled room, in individual booths (ISO 8589:2007), using covered, white ISO glasses (ISO 3591:1977) containing about 30 mL of liquid, coded with random three-digit numbers. Sessions lasted approximately 10 min. All sensory samples underwent orthonasal evaluation. The wine used for the discriminative and descriptive analyses was a 2012 Cabernet Sauvignon wine from the south of France (CS) with the following parameters measured by Fourier transform mid-infrared spectroscopy (WineScan Instrument, Foss Analytical, Hillerød, Denmark): alcohol, 12.9% (v/v); pH, 3.6; titratable acidity, 4.6 g/L as tartaric acid; and volatile acidity, 0.43 g/L. The initial concentrations of IBMP measured as described[21] and 1,4-cineole were 3.8 ng/L and 0.09 μg/L, respectively. The concentration of 1,8-cineole was below the limit of quantitation. Coded samples (Table 2) were prepared approximately 15 h prior to the session and kept at 18 °C in sealed vials to ensure chemical and sensory equilibrium. Analyses were also performed to check the solution stability between the sensory sessions. No significant loss of cineoles or IBMP was observed in either the water or wine solutions.

Sensory Panel. Judges were selected on the basis of availability and interest. A total of 16−33 volunteers participated in the various sensory panels. All panelists were research laboratory staff at the Institute of the Sciences of Vines and Wines (ISVV), Bordeaux University, and showed different levels of expertise in sensory analysis. The ages of the panelists ranged from 21 to 53 years, and the panel was comprised of between 55 and 65% females depending upon the panel.

Discriminative Analysis. Triangle tests were performed for 1,4-cineole solution samples in deionized water and CS wine. Each solution of 1,4-cineole, present at the concentrations listed in Table 2, was compared to either deionized water or the base CS wine. For each triangle test, three numbered samples (two identical and one different) were presented in a random order. Each judge used direct olfaction to identify the sample perceived as different in each test and was instructed to provide a response, even if they were uncertain of the correctness of their answer. Each triangle test was performed in duplicate.

Descriptive Analysis. The descriptive analysis focused on the impact of 1,4-cineole, in both isolation and combination with 1,8-cineole on the aromatic profile of Cabernet Sauvignon wines using an adapted version of the Deviation from Reference Method.[22] CS wine was spiked with IBMP to reach a final concentration of 10 ng/L (CSi in Table 2). This reflected the IBMP levels measured[21] in 14 wines from Margaret River and Coonawarra regions in a preliminary survey (data not shown). Additions of 1,4-cineole and 1,8-cineole were performed in the CSi wine at concentrations comparable to that found in Australian Cabernet Sauvignon wines (Table 2) and perceptible by the panel (Table 3). The tests were performed by comparing the aromatic perception of the hay, bay leaf, and blackcurrant reference

Table 3. Proportion of Positive Answers for Triangle Tests Performed in Water (Wat) and Cabernet Sauvignon Wine (CS) for 1,4-Cineole[a]

test	proportion of positive answer (%) (number of responses)	level of significance
wat + 1,4c-0.13 versus wat	38 (16)	NS[b]
wat + 1,4c-0.27 versus wat	56 (32)	$p = 0.01$
CS + 1,4c-0.13 versus CS	31 (36)	NS
CS + 1,4c-0.27 versus CS	28 (36)	NS
CS + 1,4c-0.54 versus CS	53 (34)	$p = 0.05$
CS + 1,8c versus CS	53 (36)	$p = 0.05$

[a]Sample codes are shown in Table 2. For each comparison, results were calculated by adding one and two positive sample tests. [b]NS = non-significant.

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standards (Table 4) to CSi wine that has been spiked with 1,4-cineole and 1,8-cineole (Table 2). For each test, the panel assessed the

Table 4. Descriptors and Corresponding Reference Standards Used for Descriptive Analysis

attribute	composition of the reference
bay leaf	maceration of 50 mg of commercial crumbled bay leaves for 2 min in water/wine
capsicum	solution of IBMP at 100 μg/L in water
eucalyptus	solution of 1,8-cineole at 100 μg/L in water
forest floor	maceration of 3 g of a mix of forest humus and oak leaves for 10 min in water
fresh	solution of menthol at 100 μg/L in water
hay	diluted macerate (1:3) of 500 mg of commercial hay in 100 mL in water/wine for 2 min
licorice	one licorice candy (Ricola) dissolved in 100 mL of water
spicy	500 mg of a commercial mix of ground black, red, and green pepper corns in 100 mL of water
blackcurrant	maceration of 40 g of commercial blackcurrant jam in 100 mL of water/wine for 1 min
black cherry	maceration of 40 g of commercial black cherry jam in 100 mL of water/wine for 1 min
dark fruit	maceration of 20 g of commercial blackberry jam and 20 g of blueberry jam in 100 mL of water for 10 min
red fruit	maceration of 40 g of commercial red berry fruit jam (strawberry, red cherry, and raspberry) in 100 mL of water

olfactory similarity of spiked CSi wine samples compared to the standard presented. A previous series of triangle tests had shown that a similar range of 1,4-cineole and 1,8-cineole concentrations was able to be detected by the panel (Table 3). Panelists scored the similarity between spiked wine and standard using a 10 cm scale, with the highest scores plotted on the right side of the scale (0, low; 10, high). The samples with the highest scores were perceived as most similar to the corresponding reference standard.

Multidimensional Scaling. A descriptive sorting task was used to characterize the aromatic differences between 10 Cabernet Sauvignon wines originating from the Coonawarra (n = 5) and Margaret River (n = 5) regions. Coonawarra wines were from 2010 (n = 3), 2011, and 2012 vintages, and Margaret River wines were from 2011 (n = 3), 2010, and 2012 vintages. The protocol of the sorting focused on orthonasal evaluation was as recently described.[23] The sensory description of the wine groups during the sorting task was based on 12 descriptors with appropriate reference standards that are commonly used by wine experts to describe the aroma of Australian Cabernet Sauvignon wines (Table 4). The panelists were asked to choose the most relevant terms from this list to define each group and were instructed to form between two and nine groups, with a maximum of five descriptors per group. During the session, participants had the opportunity to refresh their aroma memory by reassessing the reference standards.

Statistical Analysis. *Chemical Analysis.* The significance was examined using one-way analysis of variance (ANOVA), and the means were separated using Fisher's least significant difference (LSD) test (different letters account for significant differences at $p \leq 0.05$). ANOVA was performed using Excel software (Microsoft Corporation, Redmond, WA).

Sensory Analysis. The results of all of the triangle tests were statistically analyzed on the basis of the binomial law corresponding to the distribution of answers in this type of test (NF EN ISO 4120, 2007).

Descriptive data were analyzed using a one-way ANOVA (XLSTAT software). When more than two samples were compared, all descriptors were mean-centered per panelist and scaled to unit variance. Samples were considered as significant at $p < 0.05$. The data from multiple comparison tests were processed with a Duncan post-hoc test.

For the sorting task, dissimilarities between samples were analyzed using non-metric multidimensional scaling (MDS) as described elsewhere.[23] The analysis of 1,4-cineole, 1,8-cineole, and IBMP of the wines aimed to identify potential relationships between wine composition and the effect of regionality on aroma. The correlations between wines, attributes, and chemical compounds were plotted on a MDS map.

RESULTS AND DISCUSSION

Development and Validation of a Quantitation Method of 1,4-Cineole and 1,8-Cineole in Red Wines. Cineole isomers are symmetrical monoterpenic cyclic ethers exhibiting an epoxy-*p*-menthane structure, differing only by the position of the epoxy group (Figure 1). While 1,8-cineole has been previously quantitated in Australian red wines,[8] quantitative data for 1,4-cineole in wine have not been previously reported. However, 1,4-cineole has already been identified in red wines.[15,16] The identification of 1,4-cineole in red wines has been confirmed in the present study by the presence of peaks that displayed the identical mass spectrum of 1,4-cineole at the retention time that matched the 1,4-cineole retention index on two types of columns. The GC−MS parameters were adapted to cineole isomer analysis from a published method developed for wine volatile analysis.[19] Quantitation method validation was carried out assessing linearity, repeatability, reproducibility, limits of detection and quantitation, and recoveries in different red wines (Table 1). The standard curves obtained were linear and repeatable throughout the concentration range. The calculated limits of quantitation (LOQs) were 4 and 10 ng/L for 1,4-cineole and 1,8-cineole, respectively, and the calculated limits of detection (LODs) were 1 and 3 ng/L for 1,4-cineole and 1,8-cineole, respectively. The precision, robustness, and accuracy of the method were satisfactory for both compounds. The relative standard deviations for repeatability and reproducibility were below 7%, and recovery rates were measured at between 90 and 106% (Table 1). Interestingly, the method validation data revealed that the use of deuterated analogues was not necessary and octan-2-ol was well-adapted to HS−SPME−GC−MS analysis of 1,4-cineole and 1,8-cineole in red wines.

Survey of Cineole Isomers in Red Wines. The method was applied to analyze 1,4-cineole and 1,8-cineole in 104 commercial Australian Cabernet Sauvignon, Shiraz, and Pinot Noir wines from different regions and vintages. The results of this quantitative investigation are summarized in Table 5.

Table 5. Mean Concentrations ± Standard Deviation (SD) of 1,4-Cineole and 1,8-Cineole in Australian Cabernet Sauvignon, Shiraz, Pinot Noir Wines[a]

	Cabernet Sauvignon (n = 51)	Shiraz (n = 27)	Pinot Noir (n = 22)
1,4-cineole	0.59 ± 0.33 a	0.07 ± 0.04 c	0.22 ± 0.2 b
1,8-cineole	2.82 ± 3.26 a	1.75 ± 1.42 a	0.99 ± 0.33 b

[a]One-way ANOVA was used to compare data. Means followed by different letters in a row are significant at $p \leq 0.05$ (Fischer's LSD). All quoted uncertainty is the standard deviation of each group of wines.

Varietal Differences. 1,4-Cineole was detected in all of the wines analyzed with concentrations ranging from 0.023 to 1.6 μg/L. An important varietal effect was observed with an average concentration of 8.4- and 2.7-fold higher in Cabernet Sauvignon than in Shiraz and Pinot Noir wines, respectively (Table 5). All of the Shiraz wines exhibited concentrations below 0.2 μg/L, and 87% of Pinot Noir wines showed

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concentrations below 0.4 μg/L. Conversely, 1,4-cineole concentrations were above 0.4 μg/L in 68% of the Cabernet Sauvignon wines analyzed, including seven wines with concentrations above 1 μg/L (Figure 2). The varietal differences measured in this study between Pinot Noir and Cabernet Sauvignon will require further investigations because Pinot Noir wines originated from different regions compared to Cabernet Sauvignon wines. The 1,4-cineole/1,8-cineole concentration ratios in Cabernet Sauvignon wines ranged from 0.015 to 1.24 (Supplementary Figure 1 of the Supporting Information). The distribution of 1,4-cineole in Australian red wines was therefore very different in comparison to 1,8-cineole. These results indicate that 1,4-cineole and 1,8-cineole in wines might have different origins and suggest that the occurrence of 1,4-cineole in wine is probably not due to the presence of eucalyptus trees in the vicinity of the vineyard, as has been reported for 1,8-cineole.[9] Further studies investigating the origin of 1,4-cineole in wine are warranted.

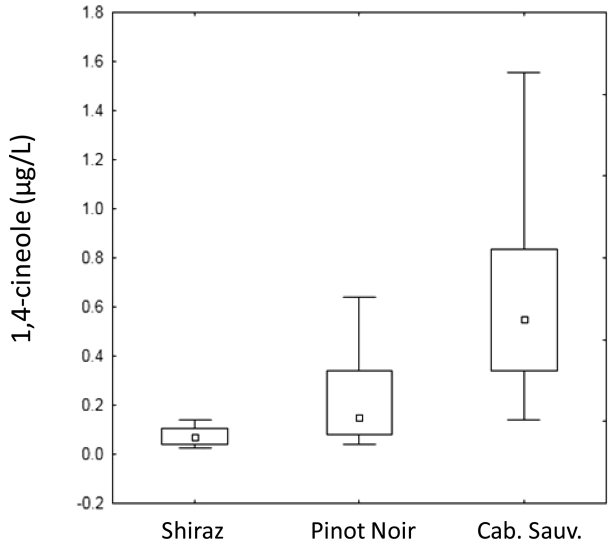

Figure 2. Distribution of 1,4-cineole concentrations in Australian red wines represented as box plots with the minimum, maximum, median, and quartiles. Cab. Sauv. = Cabernet Sauvignon.

The concentrations of 1,8-cineole were also cultivar-dependent, with higher concentrations in Australian Cabernet Sauvignon and Shiraz than Pinot Noir wines (Table 4). However, one Pinot Noir wine contained 23 μg/L 1,8-cineole. Both this wine and two Cabernet Sauvignon wines containing 19 and 66 μg/L, respectively, were considered as outliers and were not taken into account for the varietal comparison. These findings add to the uncertainty regarding the origin of 1,8-cineole in red wines and suggest that, as previously hypothesized,[5,11] factors other than proximity to eucalyptus trees may be important in determining the final concentration of this compound in wines.

Influence of the Wine Geographic Origin. Significant variations in 1,4-cineole and 1,8-cineole concentrations were measured between wines originating from different regions of Australia (Figure 3A). The Cabernet Sauvignon wines originating from Margaret River exhibited higher concentrations of 1,4-cineole than wines from Barossa and McLaren Vale ($p < 0.05$) and to a lesser extent Coonawarra ($p = 0.08$). Conversely, higher concentrations of 1,8-cineole were found in Cabernet Sauvignon and Shiraz wines produced from Coonawarra compared to Barossa and McLaren Vale ($p < 0.05$) and Margaret River to a lesser extent ($p = 0.13$) (Figure 3B). Regional variations of 1,8-cineole in Australian Cabernet Sauvignon have been previously reported.[5] The higher levels of 1,8-cineole found in the Coonawarra Cabernet Sauvignon wines are in agreement with anecdotal sensory descriptions, which include "eucalyptus" and "minty"[6] aromas, which are reminiscent of 1,8-cineole.

These results suggest that 1,4-cineole and 1,8-cineole concentrations in wine could be related to abiotic factors that characterize a terroir unit[24] (climate × soil moisture) and influence grape composition. Appropriate studies to investigate the effect of the temperature and water availability on the grape

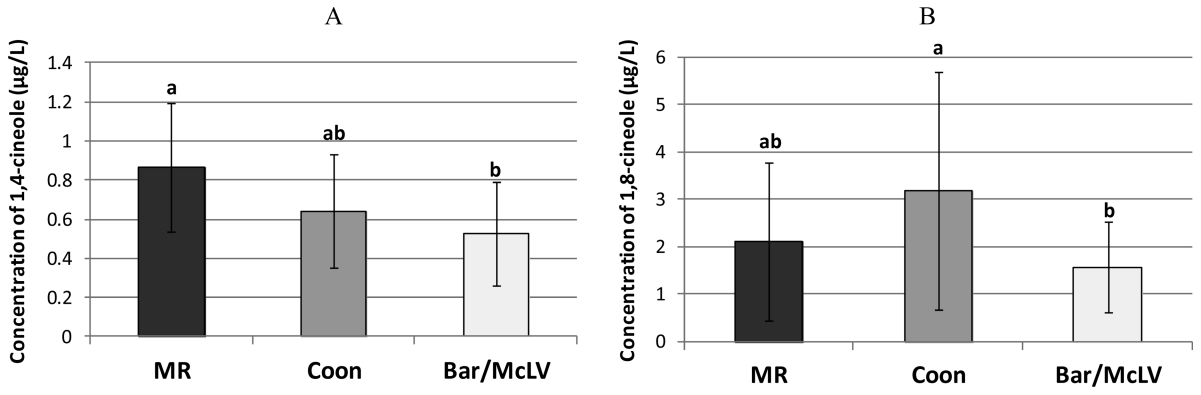

Figure 3. Effect of the geographic origin on the (A) 1,4-cineole concentration in Australian Cabernet Sauvignon wines and (B) 1,8-cineole concentration in Australian Cabernet Sauvignon and Shiraz wines. One-way ANOVA was used to compare data. Different letters on a column represent significantly ($p \leq 0.05$) different concentrations expressed in micrograms per liter. Standard errors were used for the error bars. MR, Margaret River; Bar/McLV, Barossa and McLaren Vale; and Coon, Coonawarra. The wine distribution for Figure 5A is as follows: for Margaret River, $n = 13$ with vintages as follows: 2011, $n = 9$; 2010, $n = 3$; and 2009, $n = 1$; for Coonawarra, $n = 12$ with vintages as follows: 2011, $n = 3$; 2010, $n = 7$; and 2009, $n = 2$; and for Barossa and McLaren Vale, $n = 13$ with vintages as follows: 2011, $n = 8$; 2010, $n = 4$; and 2009, $n = 1$. The wine distribution for Figure 5B is as follows: for Margaret River, $n = 17$ as follows: Cabernet Sauvignon/Shiraz, $n = 14/n = 3$ with vintages as follows: 2012, $n = 1$; 2011, $n = 11$; 2010, $n = 4$; and 2009, $n = 1$; for Coonawarra, $n = 21$ as follows: Cabernet Sauvignon/Shiraz, $n = 16/n = 5$ with vintages as follows: 2012, $n = 3$; 2011, $n = 5$; 2010, $n = 10$; 2009, $n = 2$; and 2005, $n = 1$; and for Barossa and McLaren Vale, $n = 22$ as follows: Cabernet Sauvignon/Shiraz, $n = 13/n = 9$ with vintages as follows: 2012, $n = 1$; 2011, $n = 14$; 2010, $n = 6$; and 2009, $n = 1$.

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metabolites that influence 1,4-cineole and 1,8-cineole concentrations in wines should be considered.

Sensory Characterization of Cineoles in Red Wine. *Impact Level of 1,4-Cineole in Red Wine.* The measurement of the perception threshold, performed with the ascending three-alternative forced choice (3AFC) task method, is one of the most common techniques used to evaluate quantitatively the aromatic potency of wine odorants.[25] However, recent works on perceptive interactions demonstrated, using single triangle tests, that aromatic compounds could potentially contribute to wine aromas through synergistic effects when their levels were below reported perception thresholds.[26−28] The method of single triangle tests was therefore used in the present study to check if levels of 1,4-cineole measured in Australian red wines were perceivable in water and red wines. Comparisons presented in Table 3 show that 1,4-cineole was perceived in water at 0.27 μg/L and that an addition of 0.54 μg/L in Cabernet Sauvignon wine, to produce a final concentration of 0.63 μg/L, was required before panelist perception. In comparison to the concentrations of 1,4-cineole found in the Cabernet Sauvignon wines, this suggests that 60% of the Australian Cabernet Sauvignon wines in this study had concentrations of 1,4-cineole potentially perceivable. In contrast, the average concentration of 1,4-cineole in Shiraz and Pinot Noir wines was 7- and 2.5-fold lower, respectively, than the range of concentrations potentially detectable in Cabernet Sauvignon wines. These findings suggest that 1,4-cineole has an influence on the aromatic profile of Australian Cabernet Sauvignon wines.

Sensory Characterization of 1,4-Cineole and 1,8-Cineole in Cabernet Sauvignon Wines. Descriptive analysis was undertaken to characterize the impact of 1,4-cineole in the presence and absence of 1,8-cineole on the aroma of Australian Cabernet Sauvignon wines. The presence of IBMP was also considered because this compound contributes highly to the herbaceous aroma of Cabernet Sauvignon wines investigated in this study.[2] Preliminary sensory evaluation of Cabernet Sauvignon wines with concentrations of IBMP, 1,4-cineole, and 1,8-cineole at 10 ng/L, 1.6 μg/L, and 2.5 μg/L respectively (Table 2), was performed by a small panel of five experts with extensive experience in wine aroma evaluation to generate relevant descriptors. The main sensory attributes used to describe the wines spiked with 1,4-cineole and 1,8-cineole were "hay", "dried herbs", "fresh", "mint", and "blackcurrant". The "fresh" and "minty" aromas are common characteristics of numerous Australian Cabernet Sauvignon wines to which 1,8-cineole has been previously associated.[4] Therefore, the descriptive analysis focused on the investigation of the "hay", "bay leaf", and "blackcurrant" attributes using an adapted version of the Deviation from Reference Method.[22] The ANOVA and Duncan post-hoc test showed that the addition of 1,4-cineole, both independently and in combination with 1,8-cineole, enhanced hay aromas compared to the control wine ($p < 0.05$) (Figure 4A). The intensity of bay leaf notes was significantly enhanced by the association of 1,4-cineole and 1,8-cineole ($p < 0.05$) (Figure 4B). An additional comparison showed that raising the concentrations of 1,8-cineole (10 μg/L) in this combination led to an increase in the intensity of bay leaf aromas ($p < 0.05$) (Figure 4C). In contrast, the panel was not able to significantly separate the different wines according to blackcurrant aromas, even though the addition of only 1,8-cineole tended to be perceived with more pronounced notes of blackcurrant (Supplementary Figure 2 of the Supporting Information). To check the veracity of these observations, a final comparison between the control wine and the same wine spiked with high concentrations of 1,8-cineole (10 μg/L) was

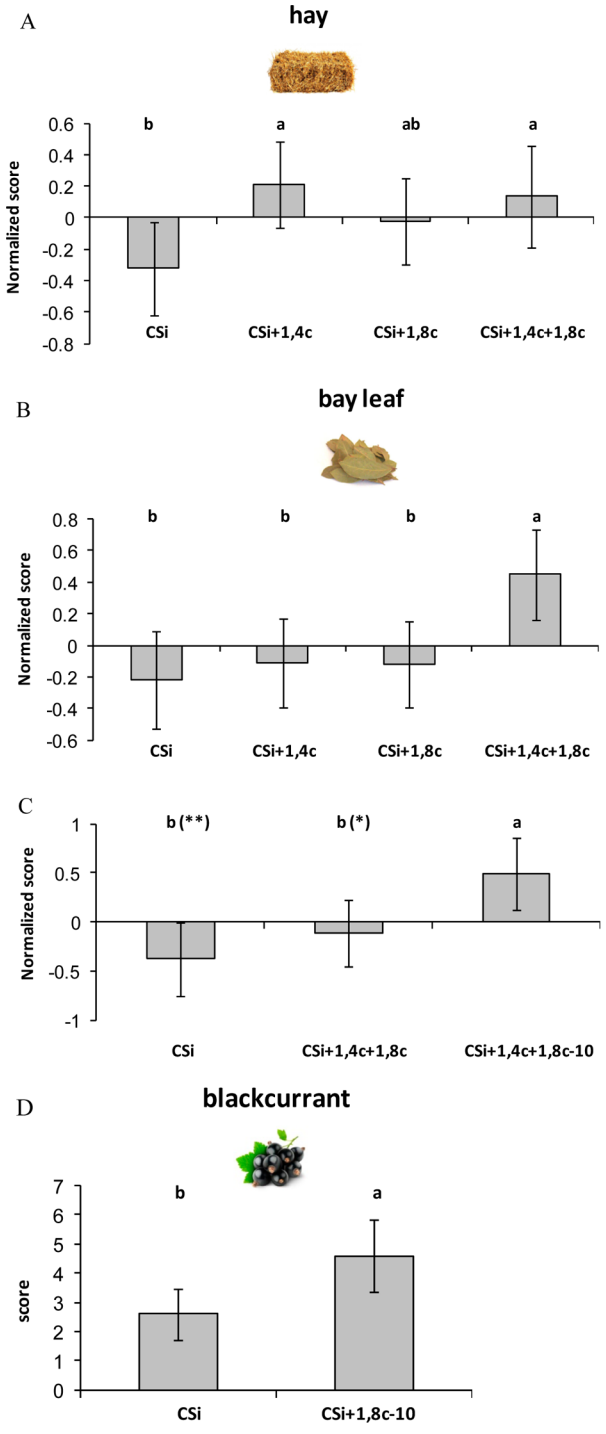

Figure 4. Descriptive analysis: evaluation of the contribution of 1,4-cineole and 1,8-cineole to (A) hay, (B and C) bay leaf, and (D) blackcurrant aromas in Cabernet Sauvignon wines using the Deviation from Reference Method (test of similarity). Sample codes are shown in Table 2. Wines and reference standards were prepared as indicated in Tables 2 and 4, respectively. The number of panelists was 33 for trials A and B and 17 for trials C and D. Results were expressed in normalized score for trials A−C and in absolute score for trial D. Standard errors measured on normalized score (A−C) and absolute score (D) were used for the error bars.

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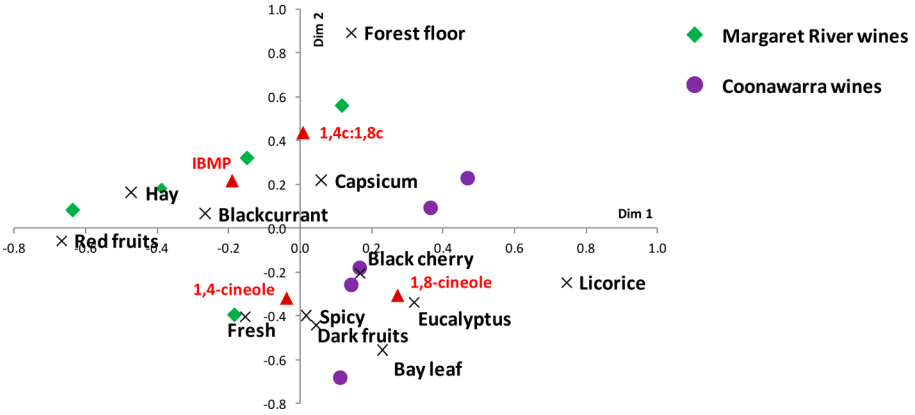

Figure 5. Two-dimensional MDS configuration of the 10 sorted Australian Cabernet Sauvignon wines from Margaret River (diamonds) and Coonawarra (circles) and correlations of the sensory terms (crosses) and chemical compounds (triangles) with the dimensions.

undertaken. The wine spiked with 1,8-cineole was perceived significantly higher for blackcurrant aromas than the control wine, confirming the previous trend ($p < 0.05$) (Figure 4D).

These findings indicate that 1,4-cineole, in both isolation and combination with 1,8-cineole, may contribute to the hay and dried herbs aromas that have been reported in Australian Cabernet Sauvignon wines. These compounds have both been reported in different aromatic herbs, such as thyme,[29] sage,[30] and bay leaf,[31] and the contribution of 1,8-cineole to the sensory perception of aromatic herbs has been reported in bay leaf and rosemary essential oils.[32,33]

While several studies have identified 1,8-cineole as a potent aroma of blackcurrant,[34,35] the current study suggests a relationship between 1,8-cineole and blackcurrant aroma in red wines. In particular, a contribution to the pronounced blackcurrant aroma in some Australian Cabernet Sauvignon wines, possibly in combination with other compounds, such as dimethyl sulfide,[36] is plausible.

Contribution of Cineole Isomers to Regional Aromas of Australian Cabernet Sauvignon Wines. The potential contribution of 1,4-cineole and 1,8-cineole to the regional typicity of Australian Cabernet Sauvignon wine aroma was investigated by comparison of Coonawarra and Margaret River wines using a sorting method. Wines were grouped according to their geographic origin (Figure 5), with Coonawarra wines associated with 1,8-cineole and attributes such as "eucalyptus", "bay leaf", "licorice", and "black cherry". These results indicate that 1,8-cineole might be an important marker of Coonawarra Cabernet Sauvignon and contribute to the eucalyptus, bay leaf, and fresh licorice aromas that are often empirically reported in these wines.[6,37] Margaret River wines were more associated with the 1,4-cineole/1,8-cineole ratio, IBMP, and descriptors such as "hay", "forest floor", "capsicum", "red fruit", and "blackcurrant". This region is generally known to produce wines with some elegant herbaceous aromas.[6,37] IBMP has been reported to contribute to green aromas perceived in Cabernet Sauvignon wines from Margaret River.[38] Even though IBMP was more correlated to Margaret River than Coonawarra wines, the concentrations measured in the present study were considerably lower (<13 ng/L) than reported in a previous work.[38] This suggests that compounds other than IBMP might contribute to Margaret River Cabernet Sauvignon typicality. The average concentrations of 1,4-cineole in Margaret River and Coonawarra wines selected for the sorting task were in the same range (0.74 and 0.69 μg/L, respectively). However, the 1,4-cineole/1,8-cineole ratios were higher in Margaret River wines and more correlated with the herbaceous attributes perceived in these wines (Figure 5).

Contrary to the descriptive analysis results, no relationship between 1,8-cineole and blackcurrant aromas was identified when the Coonawarra and Margaret River wines were compared. This lack of consistency confirms that the perception of blackcurrant aromas in red wines is complex and probably not due to only one or two compounds.[36]

The descriptors used for the sorting task were selected because they closely aligned to cineole isomers and IBMP aromas reported in the literature.[2,8] Some relationships between the sorting task and cineole isomer composition were also supported by the previously described descriptive analysis. These findings suggest that 1,4-cineole might contribute to the aromatic typicality of Margaret River Cabernet Sauvignon, when it is associated with moderate levels of IBMP and 1,8-cineole. In contrast, high concentrations of 1,8-cineole in combination with 1,4-cineole and IBMP seem to favor the expression of bay leaf aromas. A bay leaf aroma was found to be a more important descriptor for Coonawarra wines with an average concentration of 1,8-cineole of 7.7 μg/L, which was 2.9-fold higher than in the Margaret River wines. It appears that the relative concentrations of 1,4-cineole and 1,8-cineole contribute, probably with other compounds, to the regional differentiation found between Margaret River and Coonawarra Cabernet Sauvignon wines.

These results demonstrate that cineole isomers may be valuable aromatic markers for Australian Cabernet Sauvignon wines and to a lesser regional typicality. Further studies to investigate the occurrence of cineole isomers in other cultivars and wines from other important regions in the world are warranted.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.5b03847.

Distribution of 1,4-cineole/1,8-cineole concentration ratios in Australian Cabernet Sauvignon wines (Supplementary Figure 1) and descriptive analysis: evaluation of the contribution of 1,4-cineole and 1,8-cineole to blackcurrant aroma in Cabernet Sauvignon wines using the Deviation from Reference Method (test of similarity) and expressed in normalized score (33 panelists), with

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the sample codes shown in Table 2 and standard errors measured on normalized score used for the error bars (Supplementary Figure 2) (PDF)

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Notes

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