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Contribution of Dimethyl Sulfide to the Aroma of Syrah and Grenache Noir Wines and Estimation of Its Potential in Grapes of These Varieties

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The contribution of dimethyl sulfide (DMS) to the aroma of Syrah and Grenache Noir wines from the Rhone Valley of France was investigated by sensory analysis, and its levels in these wines were measured. The potential DMS in the corresponding grapes and wines, susceptible to release during wine aging, was evaluated. Free DMS and potential DMS assessed by a heat−alkaline treatment were measured in grape juices and wines by SPME-GC-MS using methods previously reported and slightly modified. A relationship between potential DMS from grapes and the total DMS levels in wine was demonstrated. Furthermore, a linear regression between the ratio of free DMS levels to these total DMS levels in wine and time of storage was found. Free and potential DMS levels in grapes and wines depended on grape variety, vintage, and vine location. DMS imparted a noticeable and complex contribution to the aroma of the wines investigated, depending on the mode of sensory perception used, either before or after glass swirling. It significantly enhanced the fruity notes of the wines, and additional truffle and black olive notes.

KEYWORDS: Aroma; wine; grape; Grenache Noir; Syrah; dimethyl sulfide; DMS; potential DMS; sensory analysis; solid-phase microextraction

INTRODUCTION

Dimethyl sulfide (DMS) is a sulfur-containing volatile compound found in a wide range of beverages and foodstuffs. It can be considered faulty or advantageous, depending on its levels, in foods of animal origin (*1*) and plant origin such as citrus fruits (*2*, *3*), melon (*4*), tomatoes (*5*), and cooked asparagus (*6*). Its levels are higher than its perception threshold in lager beer, in which *S*-methylmethionine (SMM) and dimethyl sulfoxide (DMSO) from malt were identified as its main precursors (*7*). It was found in wines of most grape varieties, with sub-parts per billion to sub-parts per million levels (*8*). However, the origin of DMS in wine is not as well documented as in beer. Several authors demonstrated the ability of yeast to release DMS during fermentation from various amino acids and derived compounds (*9*, *10*) or from DMSO (*11*). Nevertheless, its levels in freshly bottled wines are low, and they increase during aging, depending on storage temperature (*12*−*16*). Chemical pathways could produce DMS during bottle aging, either by DMSO reduction (*17*) or by SMM degradation, which would explain the release of DMS from grape juice and wine by heat−alkaline treatment (*18*). However, SMM has not been demonstrated yet as a DMS precursor in wine.

In wine, DMS often exceeds its perception threshold, 27 μg/L in red wine (*15*), particularly after aging (*14*, *15*, *19*−*21*). However, its influence on wine aroma was perceived either positively or negatively, depending on DMS level and type of wine. With regard to red wines, DMS contribution was described as positive to the aroma of a Cabernet Sauvignon red wine (*19*), as well as totally faulty at trace levels in a red Pinot wine (*21*). Wines made from Syrah grapes, and particularly aged wines, contain high DMS levels, and DMS would enhance the fruity character of these wines (*11*). However, the levels reported by different authors fell within a wide range, which could be attributed to the different analytical methods used to quantify DMS.

Due to these discrepancies reported in the qualitative and quantitative data related to DMS in different wines, as well as its origin during wine aging, our study on DMS in wine focused on Rhone Valley wines, made predominantly from the presumably DMS precursor rich Syrah cultivar and a presumably DMS precursor poor Grenache cultivar. This paper outlines the development of analytical methods for the quantitative determination of DMS and the potential DMS in the corresponding

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Table 1. Free DMS Levels in 11 Syrah and 11 Grenache Noir Wines of Various Ages and Vine Locations and Potential DMS (PDMS) Levels Assessed Using Heat–Alkaline Treatment

wine	vintage	wine storage time between fermentation and analysis (years)	wine code[a]	free DMS[b]	PDMS[b]	ratio[c] [(free DMS)/(free DMS + PDMS)]
Syrah	1992	9.5	S92a	46.0(*2*)	11(*5*)	80.7
Syrah	1996	7	S96b	15.3(*5*)	14.3(*4*)	52.0
Syrah	1998	3.5	S98c	44.5(*2*)	47.4(*3*)	48.4
Syrah	2001	2	SOld	34.7(*5*)	97.1(*5*)	26.3
Syrah	2001	2	SOle	35.1(*3*)	60.5(*3*)	36.7
Syrah	2001	2	Solf	20.3(*3*)	31.5(*6*)	39.2
Syrah	2001	2	Solg	25.3(*4*)	53.9(*4*)	31.9
Syrah	2000	1.5	sooc	11.9(*2*)	33.4(*2*)	26.3
Syrah	2002	0.5	S02e	3.7(*11*)	20.0(*3*)	15.6
Syrah	2002	0.5	SON	4.3(*5*)	22.7(*4*)	16.1
Syrah	2002	0.5	S02h	3.2(*3*)	13.7(*4*)	18.8
Grenache	1996	7	G96i	10.4(*6*)	9.8(*4*)	51.5
Grenache	1997	4.5	G97j	13.4(*4*)	14.6(*2*)	47.9
Grenache	1998	3.5	G98k	15.6(l)	19.5(l)	44.4
Grenache	2001	2	GOlm	6.5(*3*)	19.3(*5*)	25.2
Grenache	2001	2	GOln	13.8(*4*)	22.8(*2*)	37.7
Grenache	2001	2	GOlp	14.0(*1*)	27.2(*3*)	34.0
Grenache	2001	2	GOlq	6.2(*5*)	8.6(*3*)	41.9
Grenache	2000	1.5	GOOk	10.0(*5*)	26.3(*2*)	27.6
Grenache	2002	0.5	G02n	4.4(*7*)	13.7(*2*)	24.3
Grenache	2002	0.5	G02p	3.8(*3*)	22.6(*3*)	14.4
Grenache	2002	0.5	G02q	3.4(*6*)	12.1(*3*)	22.1

[a] Letters a–q encode for different vine locations (see Materials and Methods). [b] Mean levels (μg/L) and coefficient of variation in % ($n = 3$) of free DMS and PDMS. [c] Mean level of the ratio mentioned in %.

grape juices and wines, susceptible to release during wine aging. In addition, the sensory influence of DMS on the aroma of these wines was examined.

MATERIALS AND METHODS

Analytical Reagents and Supplies. K_2CO_3 and NaCl (pro analysis) were purchased from Merck (Darmstadt, Germany); tartaric acid (>99.5% pure) was purchased from Fluka (Saint-Quentin Fallavier, France) and glucose from Sigma (Saint-Quentin Fallavier, France). Sodium hydroxide (for analysis) and ethanol (absolute) were from Carlo Erba (Rodano, Italy). $[^2H]_6$-DMS (99.0 at. %) was obtained from Aldrich (Saint-Quentin Fallavier, France) and DMS (99.0% pure) from Acros Organics (Noisy-le-Grand, France). The carboxen polydimethylsiloxane (CAR/PDMS, 75 μm) SPME fibers and the manual SPME holder used for DMS analysis were purchased from Supelco (Saint-Quentin Fallavier, France). Water was purified with a Milli-Q system from Millipore S.A. (Saint-Quentin Fallavier, France).

Analytical Determination of DMS and Potential DMS (PDMS) in Grape Juices and Wines. *Grapes and Wines*. Eleven wines made from the Grenache Noir variety and 11 wines made from the Syrah variety were analyzed. Except for the 1992 Syrah wine made from grapes grown in Languedoc-Roussillon (INRA research station in Pech Rouge, southern France), all 1996−2002 wines were made from grapes grown in different locations of the Rhone Valley vineyard. These locations have been selected by the experimental winery of the Inter-Rhone research station from previous studies, to discriminate the "terroirs" found in this vineyard **(Table 1** (for example, "S92a" encodes for Syrah cultivar, 1992 vintage, vine location a). The wines were elaborated according to the Inter-Rhone standard winemaking process: Grapes were manually harvested, mechanically destemmed and crushed, and then put in 1 hL (100 L) stainless steel tanks. Musts were added with SO_2 at 4−6 g/hL depending on the acidity and sanitary state of the grapes and inoculated with 10 g/hL of L2056 commercial yeast strain (Lallemand, France). Fermentation and maceration were carried out during 7 days at 25−30 °C. After pressing, malolactic fermentation was performed with the addition of Vitilactic bacteria (Martin vialatte, France). The wines were filtered before bottling, and bottle storage temperature was 13 °C. As all of the wines were not submitted to analysis at the same time, wine age from fermentation to analysis, ranging from 0.5 to 9.5 years, was not related to vintage (**Table 1**). Due to the prejudicial sanitary state of grapes induced by the harsh 2002 climatic conditions in the Rhone Valley vineyard (heavy rains and flood), all 2002 wines were treated with an enzymatic preparation with glucanase activity, 3 g/hL (Glucanex, Novozymes). For grape juice analyses, the grapes were frozen at −20 °C immediately after harvest.

Synthetic Grape Juice and Model Base Wine. To obtain the synthetic grape juice, 220 g of glucose and 4 g of tartaric acid were added to 0.9 L of water. To obtain the model base wine, 3.5 g of tartaric acid was added to 120 mL of ethanol and 800 mL of water. The pH of both mixtures was adjusted to 3.5 with solid potassium carbonate, and their volumes were then adjusted to 1 L.

Grape Juice Preparation. Five hundred grams of berries was destemmed, defrosted at 4 °C for one night, crushed in a mixer, for 5 s at maximum power, and then filtered.

Analysis of Free DMS by Solid-Phase Microextraction (SPME). A 15 mL aliquot of wine or grape juice was transferred at room temperature to a 22 mL vial equipped with a magnetic stir bar, and 1.75 g of NaCl was added. Then 1.5 μg of $[^2H]_6$-DMS (15 μL of a 100 μg/mL solution in ethanol) was added, and the vial was sealed with a screw-top cap with a Teflon-faced septum. The solution was equilibrated by magnetic stirring at 500 rpm for 5 min. The SPME needle was then inserted through the septum, and the fiber, previously conditioned at 280 °C for 5 min, was extended into the headspace and allowed to equilibrate for 30 min with stirring at 500 rpm, at room temperature. The fiber was then retracted, removed from the vial, and immediately desorbed into the injector of the GC, with 1 min of exposure time to desorb the DMS analytes (see GC-MS conditions below). Triplicate analyses were performed on each sample.

PDMS Released by Heat−Alkaline Treatment. The analysis of wines and grape juices was carried out using the same samples analyzed for free DMS. Free DMS and $[^2H]_6$-DMS were removed from the sample by bubbling nitrogen at 100 mL/min flow rate for 10 min, with magnetic stirring at 500 rpm. PDMS was then released by performing a thermal treatment in alkaline conditions, as follows: ~300 mg of sodium hydroxide (pelletized) was added to the sample to obtain a 0.5 N solution. The vial was sealed with a new screw-top cap with a Teflon-faced septum, heated at 80 °C for 1 h, and then allowed to cool. The internal standard (1.5 μg of $[^2H]_6$-DMS solution in ethanol) was introduced into the sample through the septum and equilibrated, and

Table 2. Syrah and Grenache Noir Wines with and without DMS Addition Studied by Descriptive Sensory Analysis

wine	vintage	DMS addition (μg/L)	DMS total content (μg/L)	sample code
Syrah	2001	0	34.7	S0ld
		65.3	100	S0ld_100
		165.3	200	S0ld_200
Syrah	1996	0	15.3	S96b
		84.7	100	S96b-100
		184.7	200	S96b-200
Grenache	2001	0	6.5	G0lm
		93.5	100	G0lm_100
		193.5	200	G0lm_200
Grenache	1996	0	10.4	G96i
		89.6	100	G96i_100
		189.6	200	G96i_200

the DMS released by the reaction was quantitatively determined, as described above for free DMS. Triplicate analyses were performed on each sample.

Calibration Curves. A model base wine and a synthetic grape juice were used to obtain the calibration curves for DMS quantification in wines and grape juices, respectively. Serial dilutions in 15 mL of the model base wine or synthetic grape juice of aliquots of an ethanol solution of DMS (100 μg/mL) were made separately in the 22 mL septum-sealed glass vials used for SPME. Then 1.5 μg of $[^2H]_6$-DMS (15 μL of a 100 μg/mL solution in ethanol) was added to each dilution as internal standard. The calibration curves were obtained from these solutions by SPME analysis (see above) coupled to GC-MS. Peak area ratios (peak area of the ion *m*/*z* 62/peak area of the ion *m*/*z* 68) were plotted against the concentration ratios (micrograms of DMS/1.5 μg of $[^2H]_6$-DMS) for the following DMS concentrations: 0.15, 0.75, 1.5, 3.0, and 4.5 μg. The resultant curve was linear (response ratio = 1.1673 $\times$ concentration ratio; $R^2 = 0.9986$).

Gas Chromatography Coupled with Mass Spectrometry. GC-MS analysis was carried out using a Hewlett-Packard gas chromatograph 5890 series II fitted with a 60 m fused-silica column (0.32 mm i.d. and 1.0 μm film thickness), coated with DB5 (J&W Scientific), and connected to the injector with a 1 m deactivated fused-silica precolumn (J&W Scientific; 0.53 mm i.d.). The injector (splitless) temperature was held at 300 °C, constantly. Transfer of the sample to the GC column was accomplished by keeping the SPME fiber for 1 min in the heated chromatograph injector. The carrier gas was helium 6.0 (Linde gaz, Marseille, France), with a flow rate of 1.3 mL/min. The oven temperature program was 30 °C (for 3 min), then increased at 1 °C/min to 40 °C, and then increased at 10 °C/min to 250 °C. The GC instrument was coupled to a Hewlett-Packard 5989 A mass selective detector and a Hewlett-Packard B.05.02 MS Chemstation. The transfer line was heated at 250 °C. The electron impact (EI) energy was 70 eV, the MS source and quadrupole temperatures were set at 250 and 120 °C, respectively. The following ions in the selective ion monitoring (SIM) mode were used: *m*/*z* 62 (999) and *m*/*z* 68 (999) as quantifiers for DMS and $[^2H_6]$-DMS, respectively; *m*/*z* 45 (405), 47 (875), and 61 (308) and *m*/*z* 48 (354), 50 (972), and 66 (275) as qualifiers for DMS and $[^2H_6]$-DMS, respectively.

Sensory Analysis. *Wines*. Four of the 22 wines submitted to instrumental analysis were used as base wines for the study of DMS sensory contribution (1996 and 2001 Syrah wines, 1996 and 2001 Grenache Noir wines, coded S96b, S01d, G96i, and G01m, respectively, in **Table 1**). Each was divided into three portions: *first portion*, natural wine; *second portion*, wine spiked with DMS to a total level of 100 μg/L; *third portion*, wine spiked with DMS to a total level of 200 μg/L (**Table 2**). Thirty-three additional Grenache Noir and Syrah wines, 2−9 years old, made with grapes grown in various locations of the Rhone Valley vineyard were used during the tasting sessions for panel training.

Sensory Analysis Protocol. The sensory analyses were performed in the Inter-Rhone sensory analysis laboratory. Wine samples (25 mL), stored at 4 °C, were presented at 17 °C, in random order, in coded (with a three-digit number) tulip-shaped glasses covered by Petri dishes.

Table 3. Final Aroma Attributes Used in the Sensory Descriptive Analysis of Grenache Noir and Syrah Wines

black currant	vanilla	undergrowth
strawberry/raspberry	fresh vegetable	licorice
jam	dried vegetable	cocoa
candied fruits	garrigue	toasted
fruits in alcohol	black olive	animal (leather)
dried fruits	pepper	truffle

The olfactory evaluation of the wines was performed by direct (orthonasal) perception. First and second perceptions were differentiated, before and after glass swirling, respectively.

Panel Training. The panel of judges consisted of 20 persons from Inter-Rhone research station, selected on the basis of previous experience in wine tasting. The judges were trained in eight sessions, according to the methodology described by NFV 09-021 norm for quantitative descriptive analysis (QDA). First and second sessions were used to test and train the panel at identifying and scoring the perception magnitude (using a seven-point scale) of 10 red wine aroma descriptors, with natural aroma standards and aromatized wines. In the third session, a list of aroma attributes was freely generated by the panel, using direct olfaction of five Syrah wines and five Grenache Noir wines, of 1994−1998 vintages. This list, consisting initially of 355 terms, was reduced to 73 terms by eliminating, in consensus with the panel, nonconvenient terms. Terms quoted fewer than three times were also eliminated. In the fourth session, the panel evaluated the presence or absence of these 73 odor attributes in eight wines; terms quoted fewer three times for one wine and terms considered to be redundant by the panel were eliminated, which led to the consensual reduction of the list to 26 attributes. In the fifth session, the panel validated commercial aroma standards as references for the 26 attributes and was trained at memorizing these references. In the sixth session, the panel was trained at scoring the magnitude of the 26 odor attributes by the olfactory evaluation of eight wines (four Grenache Noir and four Syrah wines), using a category scale from 0 (no perception) to 7 (highest perception). The data were used to select the most relevant attributes from the correlation matrix and the comparison of geometrical means (GM) [GM is the square root of the product of the frequency quotation (*F*) with the relative intensity (*I*): $GM = (F \times I)^{1/2}$ (*22*)], which established, in consensus with the panel, a final list of 18 attributes (**Table 3**). In the seventh and eighth sessions, the panel was trained and tested at memorizing the odor standards and at scoring the magnitude, using a restricted (from no perception to highest perception) but nongraduated scale, of the 18 descriptors in seven wines, with duplication of three wines. Its repeatability and homogeneity were checked using variance analysis. In the ninth session, the panelists scored the magnitude of the 18 attributes, before and after glass swirling, in the 12 experimental samples (**Table 2**).

Data Acquisition and Treatment. Data acquisition and statistical treatments were performed using Fizz software (Biosystèmes, Dijon, France). Two-way (samples $\times$ judges) analyses of variance (ANOVA), associated with Duncan tests, were performed on sensory means to test individual reproducibility, panel homogeneity, and the differences between wines for each attribute. Principal component analyses were performed to illustrate the main differences and similarities among samples.

RESULTS AND DISCUSSION

SPME Analysis of Free and Potential DMS. Due to the role of DMS in the global sulfur cycle and food flavor, many methods have been developed for its analysis (*12*, *15*, *20*, *21*,*23*). The headspace solid-phase microextraction (HS-SPME) used for the quantitative analysis of DMS in beer (*24*) and in wine (*25*) was chosen, as it was sensitive, selective, and rapid. To circumvent the problems reported by Murray (*26*), a stable isotope dilution assay was used, as reported previously for analyzing DMS in seawater, with high isotopic purity commercial $[^2H_6]$-DMS as labeled internal standard (*27*). GC-EIMS,

used in the SIM mode, gave selective and sensitive detection of DMS and [$^2H_6$]-DMS. For the Syrah and Grenache samples, analyzed in this study, the DMS detection limit was 2.0 μg/L in the wines and 0.1 μg/L in the grape juices with an estimated signal/noise ratio of 3:1. The repeatability, estimated by the coefficient of variation for three replicates of each sample, was <6% for most analyses (**Tables 1** and **4**).

Determination of PDMS. DMS can be chemically produced from a variety of organosulfur precursors (*28*), but in terrestrial plants it appears to be derived mainly from *S*-methylmethionine, a sulfonium compound assumed to correspond to a storage and transport form of methionine (*29*). Thus, in beer, it was established that DMS is formed by thermal degradation of *S*-methylmethionine during the kilning and brewing steps of the brewing process (*7*, *30*). That is why the thermal treatment in alkaline conditions, generating DMS from SMM, is routinely performed for the determination of potential DMS in materials related to beer production (*31*, *32*). It was also applied as an indirect method for the analysis of SMM in citrus fruits, to control DMS appearing during citrus juice processing (*33*). In the winemaking process, DMS can also be formed from DMSO and other sulfur-containing compounds by yeasts during fermentation (*11*), but the temperature conditions throughout the winemaking process are far lower than 60 °C, which is the reported minimal temperature for thermal degradation of SMM (*34*), and the occurrence of SMM in grape juice or wine has yet to be proved. However, Swan (*18*) found that DMS was formed when applying the SMM alkaline decomposition reaction to wines, suggesting that the levels of released DMS could gauge the potential for DMS release during storage. Indeed, in the same conditions, the other possible precursors could give rise to DMS (*28*). The procedure was adapted to the SPME technique used for free DMS analysis. Thus, to take care of the high volatility of DMS and to limit possible loss of the released DMS, the alkaline reaction was conducted in the analysis vial itself. At the end of the reaction, [$^2H_6$]-DMS was added through the septum and equilibrated in solution, and the fiber was introduced directly into the vial headspace. The vial sealing (with screw-top caps with Teflon-faced septa) appeared to be appropriate to the conditions used, because the repeatability of PDMS analysis, estimated by the coefficient of variation for three replicates of each sample, was similar to that of free DMS (**Tables 1** and **4**). Before the alkaline reaction was begun, free DMS and internal standard were totally stripped from the sample by nitrogen purging. The stripping efficiency was validated by performing analysis before and after purging and was consistent with previous works (*35*).

Analytical Study. *Wines.* In the 11 Syrah and 11 Grenache wines, 0.5−9.5 years aged (vintages 1992−2002), free DMS levels ranged from 6 to 46 μg/L (**Table 1**), much lower than those measured in California, Australia, or New Zealand wines, which had up to 900 μg/L (*19*, *36*). The DMS levels were significantly higher in the Syrah than in the Grenache wines (one-way ANOVA; $F_{1,\ 20} = 6.5$, $p = 0.025$). In half of the former ones, DMS levels exceeded 27 μg/L, which was the odor threshold reported in red wine by Anocibar Beloqui (*15*), whereas they were lower in the latter ones. DMS could therefore particularly contribute to Syrah wine aroma.

On the other hand, the range of PDMS levels in these 22 wines was wider, from 8.6 to 97.1 μg/L (**Table 1**). As for free DMS, the PDMS levels were significantly higher in Syrah than in Grenache wines (one-way ANOVA; $F_{1,\ 20} = 5.6$, $p = 0.037$), which is indicative of a possible relationship between PDMS and free DMS. The differences observed in the levels of both free DMS and PDMS in the four 2001 Syrah wines, on the one hand (S01d, S01e, S01f, S01*g* in **Table 1**), and in the four 2001 Grenache wines (G01m, G01n, G01p, G01q in **Table 1**), on the other hand, differing only in the vineyard location, showed that the influence of the vineyard location was statistically significant in each varietal group (for the four one-way ANOVAs, $F_{3,\ 8} = F > 75$ and $p < 0.0001$). With regard to the variations of free DMS in wine with aging, an upward trend was observed in some previous work (*11*−*13*, *17*), whereas no trend was reported by others (*19*, *36*). It has to be noted that the wine samples analyzed in this study were wines of different vintages and ages, but not the same wines sampled at different aging times (**Table 1**). That could explain why no significant regression of free DMS levels and PDMS levels with age was observed. Nevertheless, a linear regression of the ratio [free DMS/(free DMS + PDMS)] with bottle aging was observed ($F_{1,20} = 126$, $p = 0.001$) **(Figure 1)**. That could be explained by the release of DMS from PDMS during wine aging, showing that the assay proposed by Swan (*18*) was a good model to gauge the potential for DMS release during storage. The increase of the proportion of free DMS relative to the sum (free DMS + PDMS) was ∼10% every two years. Hence, without excluding other precursors (*28*), the most probable DMS precursor in grape would be SMM, although the minimum temperature for thermal degradation of SMM was found to be 60 °C (*34*). Temperature conditions of wine aging are far lower, which could explain why little work has been devoted to this potential precursor in wine. However, SMM was more recently found to spontaneously degrade in a cheese model medium, at low temperature (*37*).

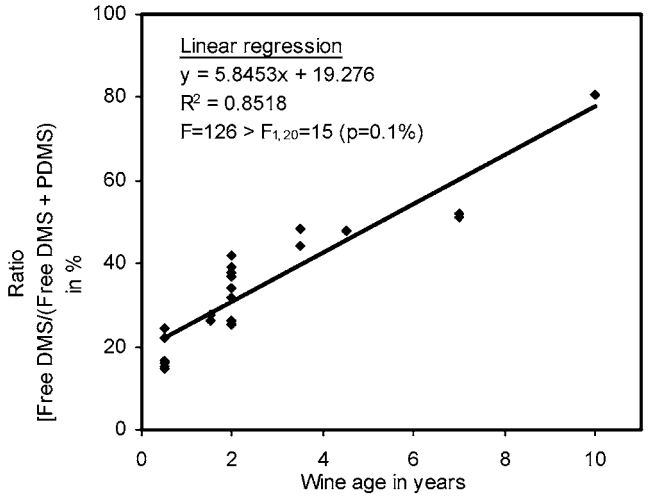

Figure 1. Linear regression between ratio [free DMS/(free DMS + PDMS)] and age for the 11 Syrah and 11 Grenache Noir wines of **Table 1**.

Grape Juices. The analytical method described above to measure free DMS in grape juices gave free DMS levels of <5 μg/L in the Syrah and Grenache grape juices shown in **Table 4**, but PDMS released by heat−alkaline treatment from these grape juices ranged from 12 to 264 μg/L **(Table 4)**. For both vintages, PDMS tended to be higher in Syrah than in Grenache grape juices, which was consistent with the variety specificity already observed for free DMS and PDMS in wines, but the differences were not highly significant (for 2001 vintage, $F_{1,4} = 5.7$, $p = 0.12$; for 2002 vintage, $F_{1,2} = 73$, $p = 0.07$). Indeed, the PDMS levels in the 2001 grape juices shown in **Table 4** were highly dependent on vine location in each varietal group ($F_{3,8} > 172$, $p < 0.001$), which produced high variability within each group. In addition, the PDMS levels for each of the 2001/

Table 4. Potential DMS (PDMS) Levels in Syrah and Grenache Noir Grape Juices of Various Vine Locations Assessed Using Heat–Alkaline Treatment and Free DMS Levels in the Corresponding Wines[a]

grape variety	harvest year	PDMS in grape juice[b]	wine code[c]	free DMS in the corresponding wine[b]
Syrah	2001	141.6 (*4*)	SOle	35.1(*3*)
Syrah	2001	263.8(f)	Solf	20.3(*3*)
Syrah	2001	99.7(*6*)	Solg	25.3(*4*)
Syrah	2002	46.4(*5*)	S02f	4.3(*5*)
Syrah	2002	46.0(*4*)	S02h	3.2(*3*)
Grenache	2001	55.4(*5*)	GOln	13.8(*4*)
Grenache	2001	62.5(*4*)	GOlp	14.0(*1*)
Grenache	2001	22.0(*4*)	GOlq	6.2(*5*)
Grenache	2002	12.2(*5*)	G02n	4.4(*7*)
Grenache	2002	19.3(*4*)	G02p	3.8(*3*)

[a] All free DMS levels detected in these grape juices ranged from 0.3 to 4.6 μg/L. [b] Mean levels (μg/L) and coefficient of variation ($n = 3$) of PDMS and free DMS in %. [c] Letters a–q encode for different vine locations (see Materials and Methods and **Table 1**).

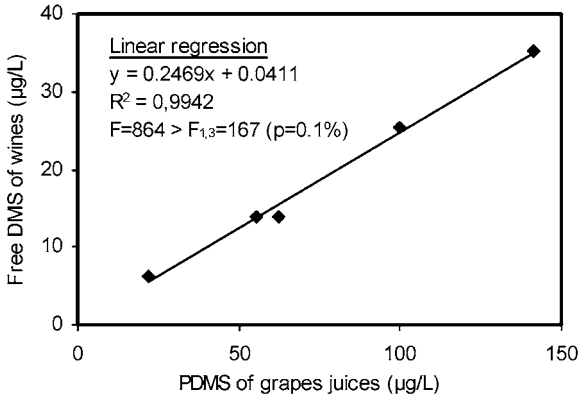

Figure 2. Linear regression between free DMS in five 2001 Grenache Noir and Syrah wines (S01e, S01g, G01n, G01p, G01q) and PDMS, as DMS released by heat–alkaline treatment of the grape juices made with the corresponding grapes (data from **Table 4**). Sample S01f was not correlated (see text).

2002 pairs of grape juices from three vine locations, (S01f, S02f), (G01n, G02n), and (G01p, G02p) (see **Table 4**), were statistically different in each vine location group (for the three ANOVAs, $F_{1,4} > 692$, $p < 0.0005$), with a decrease by 70−80% in 2002. It must be noted that 2002 climatic conditions were harsh in the Rhone Valley vineyard (heavy rains and flood), inducing premature state of the grapes at harvest. These 2001/2002 differences were similarly observed in the levels of both free DMS and PDMS for the five wine pairs (S01e, S02e), (S01f, S02f), (G01n, G02n), (G01p, G02p), and (G01q, G02q) (see **Table 1**; for the 10 ANOVAs, $F_{1,4} > 19$, $p < 0.05$). However, for the wines, these differences included not only the influence of the vintage but also that of the time of storage (2001 wines were 2 years aged, whereas 2002 wines were 0.5 year aged at analysis, see **Table 1**).

Furthermore, a good linear regression between the free DMS levels in the 2001 wines (Syrah and Grenache, 2 years aged) and the PDMS in the corresponding grape juices was observed (**Figure 2**). A similar linear regression was also observed between the DMS total level (free DMS + PDMS) in wines and the PDMS in grape juices (**Figure 3**), which was consistent with the relationship linking free DMS and PDMS in wines with storage time, as discussed above. The DMS total level (free DMS + PDMS) in wines never accounted for >70% of PDMS

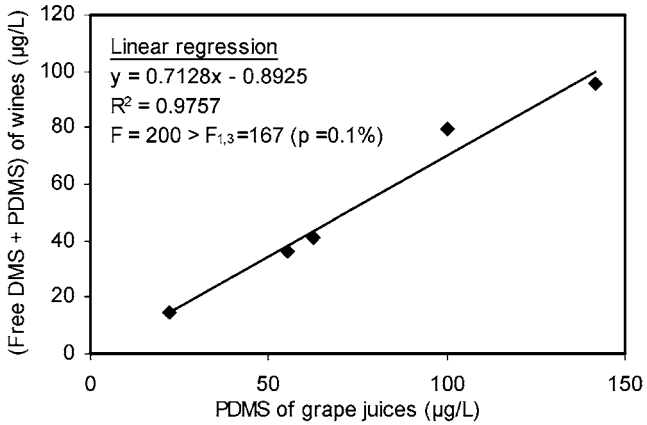

Figure 3. Linear regression between the total (free DMS + PDMS) in five 2001 Grenache Noir and Syrah wines (S01e, S01g, G01n, G01p, G01q) and PDMS, as DMS released by heat–alkaline treatment, of the grape juices made with the corresponding grapes (data from **Tables 1** and **4**). Sample S01f was not correlated (see text).

in grape juices, which suggested a partial loss of DMS during the winemaking process and aging. That was surprising as it was previously reported that DMS was formed during fermentation by *Saccharomyces cerevisiae* yeasts from amino acids or derivatives such as cystine, cysteine, glutathione, and *S*-adenosylmethionine (*9*, *10*) or by enzymatic reduction of DMSO in beer (*7*) and wine (*11*). These compounds should not release DMS by heat−alkaline treatment, as presumed from their chemical structure and probable reactivity in such conditions, and thus could not be included in the PDMS. On the other hand, *S*-methylmethionine, which could be a PDMS candidate (*7*, *38*), was not metabolized by *S. cerevisiae* yeasts (*9*), but could partially be converted into DMS by chemical pathways (*37*) occurring during fermentation. Indeed, the temperature during red wine fermentation is higher (25−30 °C) than during aging (13 °C). The DMS formed by this chemical process and by yeasts would be purged from the fermentation medium by CO_2 stripping. These phenomena could account for the low DMS levels usually measured in freshly bottled wines (*11*, *21*). In this study, one grape juice presented an atypical behavior (Syrah 2001, with S01f coding for the corresponding wine in **Table 4**): the DMS total level measured in the corresponding wine accounted for only 20% of the grape juice PDMS, instead of the 70% observed for the five others, and was not included in the linear regression. This could arise from higher DMS loss during fermentation, which could be explained by the headspace volume that took up 93% of the fermentation tank for this sample, as very few grapes were available, whereas it took up 54−74% for the five other samples.

From the relationships between grape juice PDMS and wine free DMS, it can be concluded that grape juice PDMS levels determined by heat−alkaline treatment appears to be a useful parameter for the enologist to predict DMS levels in the corresponding wine. The determination of PDMS at wine bottling could also be useful for the evaluation of the aging time for the wine to reach DMS levels contributing positively or negatively to aroma. However, it has to be kept in mind that other reported potential precursors in wine susceptible to the release of DMS during wine aging, such as DMSO (*11*, *17*), were not taken into account by this method, as heat−alkaline treatment was not suitable to reduce DMSO to DMS. On the other hand, strong alkaline conditions could induce further transformation of DMS precursors, resulting in a loss of DMS.

Table 5. Variance Analysis and Duncan Test of the Effect of DMS Addition on the Odor Attributes at First Perception for Each Syrah (S96b; S01d) and Grenache (G96i; G01m) Wine

attribute[a]		S96b	S96b	G96i	G01m
truffle	*P*[b]	0.01%	0.01%	0.01%	0.01%
	control[c]	C[d]	B	C	B
	100	B	A	B	A
	200	A	A	A	A
black olive	*P*	2.44%	0.01%	0.36%	0.72%
	control	B	C	B	B
	100	A	B	A	A
	200	A	A	A	A
undergrowth	*P*	0.01%	0.27	0.01%	0.01%
	control	C	B	B	B
	100	B	A	A	A
	200	A	A	A	A
black currant	*P*	NS	4%	NS	2.14%
	control		A		A
	100		AB		AB
	200		B		B
jam	*P*	NS	2.37%	0.01%	NS
	control		B	A	
	100		A	B	
	200		A	B	
candied fruits	*P*	NS	NS	2.72%	NS
	control			A	
	100			B	
	200			B	
fruits in alcohol	*P*	NS	2.28%	1.70%	NS
	control		B	A	
	100		A	B	
	200		A	B	
dried fruits	*P*	NS	NS	NS	0.07%
	control				B
	100				A
	200				A
vanilla	*P*	NS	NS	0.20%	NS
	control			A	
	100			B	
	200			B	
dried vegetable	*P*	NS	NS	1.0%	1.64%
	control			A	B
	100			B	A
	200			B	A
toasted	*P*	NS	NS	2.42%	NS
	control			A	
	100			AB	
	200			B	
animal (leather)	*P*	NS	NS	2.09%	0.48%
	control			B	B
	100			B	A
	200			A	A

[a] Addition of DMS produced no statistically significant effect on the other six odor attributes of the final list used (see **Table 3**). [b] Level of significance of ANOVA. NS = not significant ($P > 0.05$). [c] For each wine mentioned in the columns: control = wine without DMS addition; 100 and 200 = wine spiked to get 100 and 200 μg/L of DMS, respectively (see **Table 2**). [d] For each wine and each attribute, samples rated at different intensities by the Duncan test were given different letters: A, B, C = higher, medium, lower intensity of the attribute, respectively.

In this study, carbon disulfide and methanethiol were identified among the numerous products of heat−alkaline treatment applied to wines. Nevertheless, they were not promoted when such treatment was applied to grape juices, which suggested that they had precursors other than those of DMS. In addition, whatever the predictive tool, the high volatility of DMS may affect its actual evolution and make it sensitive to fermentation and storage conditions (*39*), as discussed above.

Table 6. Variance Analysis and Duncan Test of the Effect of DMS Addition on the Odor Attributes at Second Perception (after Glass Swirling) for Each Syrah (S96b; S01d) and Grenache (G96i; G01m) Wine

attribute[a]		S96b	S01d	G96i	G0lm
truffle	*P*[b]	0.29%	0.04%	0.03%	0.01%
	control[c]	B[d]	B	B	C
	100	A	A	A	B
	200	A	A	A	A
black olive	*P*	NS	0.03%	1.88%	1.54%
	control		C	B	B
	100		B	AB	A
	200		A	A	A
black currant	*P*	1.27%	NS	NS	3.36%
	control	B			B
	100	A			A
	200	A			A
jam	*P*	2.50%	NS	NS	2.66%
	control	B			A
	100	A			B
	200	A			A
strawberry/raspberry	*P*	0.23%	NS	NS	NS
	control	B			
	100	A			
	200	A			
fruits in alcohol	*P*	NS	0.87%	NS	NS
	control		B		
	100		A		
	200		A		
dried vegetable	*P*	NS	NS	0.01%	NS
	control		A		
	100		B		
	200		C		
garrigue	*P*	NS	0.06%	NS	NS
	control		B		
	100		B		
	200		A		

[a] Addition of DMS produced no statistically significant effect on the other 10 odor attributes of the final ones used (see **Table 3**). [b] Level of significance of ANOVA. NS = not significant ($P > 0.05$). [c] For each wine mentioned in the columns: control = wine without DMS addition; 100 and 200 = wine spiked to get 100 and 200 μg/L of DMS, respectively (see **Table 2**). [d] For each wine and each attribute, samples rated at different intensities by the Duncan test were given different letters: A, B, C = higher, medium, lower intensity of the attribute, respectively.

Sensory Descriptive Analysis of Wines Supplemented with DMS. *Panel Training and Generation of Descriptive Attributes.* At the beginning of the tasting sessions, the panel's performances were statistically tested, using ANOVA, which showed that individual and group performances were satisfactory in terms of identification and repeatability, but revealed a heterogeneous use of the scoring scale and the absence of group consensus on the descriptive attributes. The term-generating step resulted in an initial list of 355 descriptive attributes of Syrah and Grenache Noir wines. The list was reduced in three steps to 18 attributes. The first reduction, from 355 to 73 terms, was based on the elimination of the less frequently quoted descriptors and of nonconvenient terms such as gustative attributes (e.g., "sweet"), hedonistic terms (e.g., "unpleasant"), imprecise terms (e.g., "red fruits"), and scoring terms (e.g., "strong", "weak"). In the second reduction step, from 73 to 26 attributes, the panel selected the most relevant attributes for eight wines and operated groupings of terms that it could not differentiate (e.g., "raspberry" and "strawberry" grouped under "raspberry/strawberry"; "animal" and "leather" grouped under "animal"). The last reduction step was based on two techniques: the comparison of the geometrical means (GM) led to the elimination of the

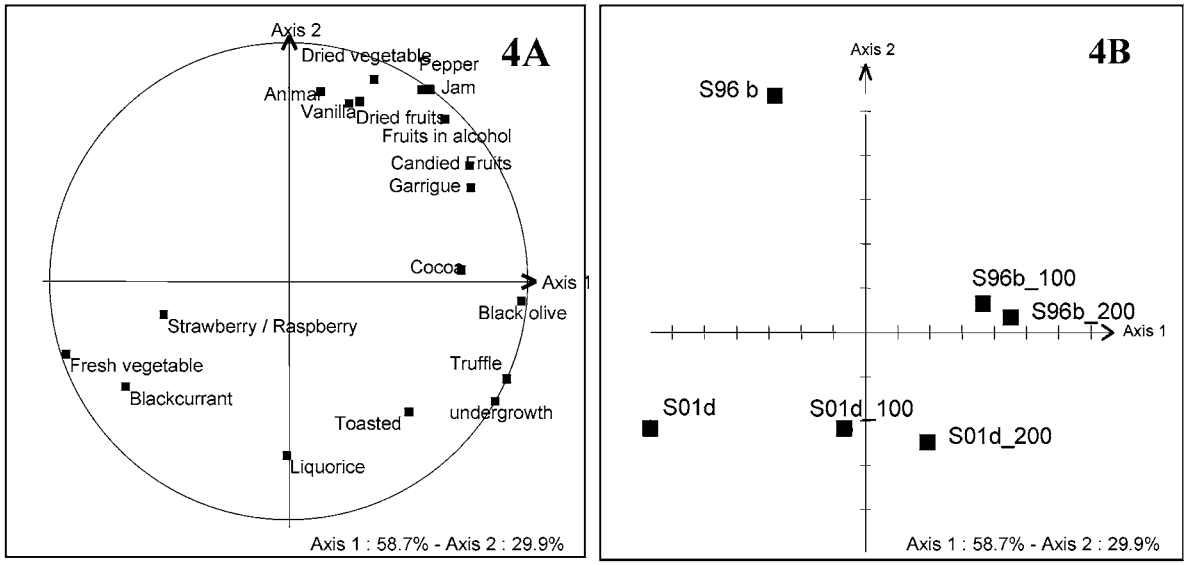

Figure 4. Projection of the Syrah wines with and without DMS addition (**Table 2**) and sensory variables (**Table 3**) on the first two axes of the PCA carried out using the olfactory profiles at first perception (without glass swirling): (**A**) correlation circle; (**B**) projection of samples; (■) samples significantly represented on the first plane (sum of squared correlation coefficients on the two first axes higher than 0.5); (□) samples not significantly represented on the first plane (sum of squared correlation coefficients on the two first axes lower than 0.5).

attributes "honey/caramel", "sweet spices", and "citrus fruits", and some highly correlated descriptors in the correlation matrix were grouped, in consensus with the panel (e.g., "undergrowth", "mushroom", and "woody" grouped under "undergrowth"; "prune" and "jam" grouped under "jam"; "cherry", "blackberry", and "raspberry/strawberry" grouped under "raspberry/strawberry"). After a final training step, the panel was tested, and the results showed that it had reached satisfactory qualities of homogeneity and repeatability regarding the use of the attributes and the use of the scoring scale. The final list consisted of 18 attributes (**Table 3**).

Sensory Descriptive Analysis of Wines with and without DMS Addition. Previous work showed that the influence of DMS on wine aroma depended not only on DMS concentration but also on the type of wine, meaning grape variety and age (*11*−*13*, *21*, *40*). This work aimed at evaluating the effect of DMS on the overall aroma of Grenache Noir and Syrah wines, using four wines previously studied in the analytical part (1996 and 2001 Syrah wines, 1996 and 2001 Grenache Noir wines, coded S96b, S01d, G96i, and G01m, respectively, in **Table 1**) spiked with DMS to attain three levels (natural level, 100 μg/L, and 200 μg/L). The 12 resulting samples (**Table 2**) were submitted to sensory descriptive analysis by direct olfactory evaluation, with differentiation between first perception and second perception (before and after glass swirling, respectively). The descriptive profiles, defined as the average magnitudes of the 18 odor attributes of the final list (**Table 3**), were submitted to variance analyses coupled with Duncan tests, to test the effect of DMS addition on each odor attribute for each wine (**Tables 5** and **6**). The effect of DMS addition on the first olfactory perception was statistically significant ($p > 0.05$) for 12 attributes in at least one wine (**Table 5**). It was mainly characterized by the increase of the intensity of the attributes "black olive", "truffle", and "undergrowth", which was statistically different for the four wines. These attributes are usually considered as bouquet attributes of aged Côtes-du-Rhône wines. Moreover, except for the 1996 Syrah wine (S96b), DMS addition induced other changes in the first olfactory perception, depending on the wine. Thus, when spiked in the two Grenache wines G96i and G01m, DMS increased the first perception of the "animal" attribute but decreased that of the "black currant" note when spiked in the two youngest wines, either Grenache or Syrah (G01m and S01d). The "jam" and "fruits in alcohol" attributes decreased when DMS was spiked in the 1996 Grenache wine (G96i) but increased when added to the 2001 Syrah wine (S01d). Only in some cases, as for the attributes "black olive", "truffle", and "undergrowth", did the olfactory effect of DMS increase with DMS level (100 g/L and 200 μg/L).

With glass swirling, the effect of DMS addition was modified, as shown after statistical treatment by ANOVA and Duncan tests (**Table 6**). Eight attributes differentiated the wines spiked with DMS from the control wines. As for first perception, "truffle" and "black olive" notes were still enhanced in all of the four spiked wines, but "undergrowth" was no longer discriminated. Moreover, the addition of DMS increased the intensity of at least one of the fruity attributes in at least one of the three wines, S96b, S01d, G01m, and the sensory effect of the two DMS levels was not differentiated: "fruits in alcohol" increased in S01d, "jam" and "black currant" in G01m and S96b, and "strawberry/raspberry" in S96b. Thus, except for the 1996 Grenache wine G96i, DMS addition globally emphasized the fruity character of the wines. Finally, when spiked to the 2001 Syrah wine (S01d), DMS additionally increased the "garrigue" attribute (mediterranean semi-arid shrubby land with main odors of thyme and rosemary).

Principal component analyses (PCAs) were performed to display graphically the effects of DMS addition for all 18 attributes on the first olfactory perception of Syrah wines (**Figure 4**) and Grenache wines (**Figure 5**) and on the second olfactory perception of the same Syrah (**Figure 6**) and Grenache samples (**Figure 7**). In the following discussion, the variables presenting squared correlation coefficients to the first plane less than 0.60 will not be considered. At first perception, "black olive", "truffle", and "undergrowth" notes were positively correlated to the first axis of both PCAs (**Figures 4A** and **5A**), thus separating the wines spiked with DMS from the control wines, and, to a lesser extent, the two levels of added DMS for each wine (**Figures 4B** and **5B**). This observation was not significant for samples S01d_100 and G01m_100, as their squared correlation coefficients to this axis were low (0.02 and

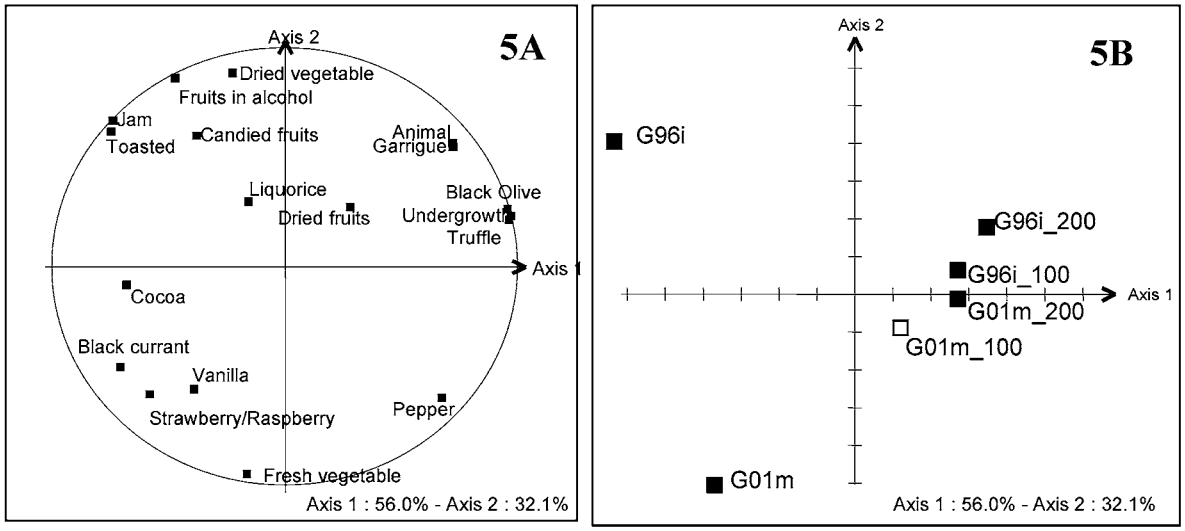

Figure 5. Projection of the Grenache Noir wines with and without DMS addition (**Table 2**) and sensory variables (**Table 3**) on the first two axes of the PCA carried out using the olfactory profiles at first perception (without glass swirling): (**A**) correlation circle; (**B**) projection of samples; (■) samples significantly represented on the first plane (sum of squared correlation coefficients on the two first axes higher than 0.5); (□) samples not significantly represented on the first plane (sum of squared correlation coefficients on the two first axes lower than 0.5).

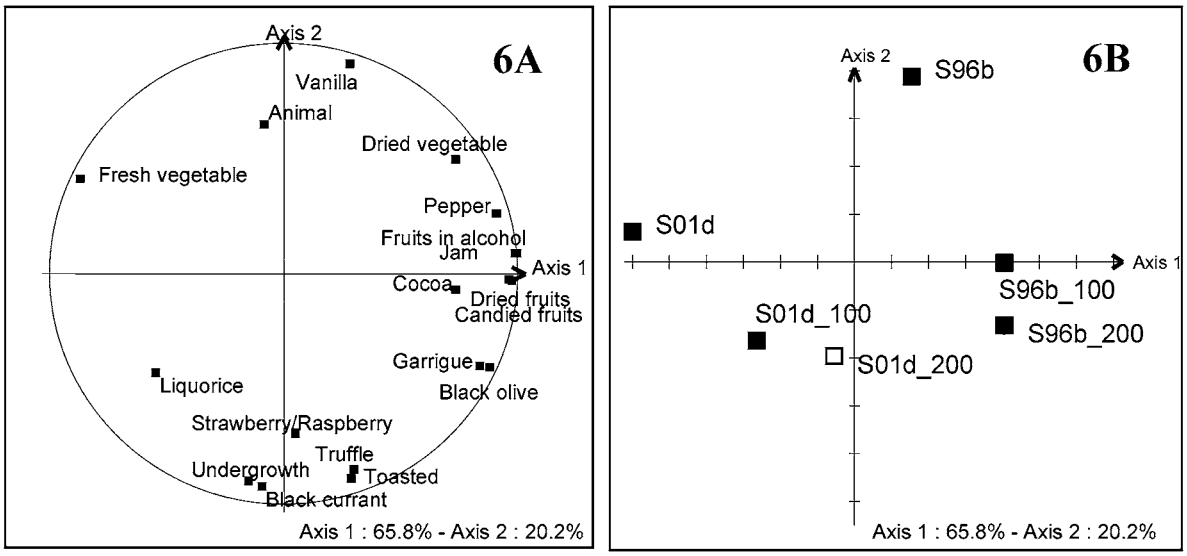

Figure 6. Projection of the Syrah wines with and without DMS addition (**Table 2**) and sensory variables (**Table 3**) on the first two axes of the PCA carried out using the olfactory profiles at second perception (after glass swirling): (**A**) correlation circle; (**B**) projection of samples; (■) samples significantly represented on the first plane (sum of squared correlation coefficients on the two first axes higher than 0.5); (□) samples not significantly represented on the first plane (sum of squared correlation coefficients on the two first axes lower than 0.5).

0.13, respectively). For Syrah samples **(Figure 4)**, "fresh vegetable" and "black currant" were negatively correlated to the first axis, which illustrated that DMS addition decreased the intensity of these attributes characterizing the initial wines. In both PCAs, the second axis mainly separated the 1996 and 2001 control wines. Attributes related to the aged wines S96b and G96i of the two varieties, such as "jam", "fruits in alcohol", "dried vegetable", and, additionally, "candied fruits" for S96b, were positively correlated. On the other hand, "fresh vegetable", describing the young aroma of the G01m control, was negatively correlated to axis 2. Representation of the samples in the first planes of PCAs **(Figures 4B** and **5B)** showed that, at first perception, DMS addition induced dominant "black olive", "truffle", and "undergrowth" notes (axis 1). The olfactory differences between young and old wines were consequently lessened (axis 2). It is noted that this latest observation was not significant for samples G01m_100 and G96i_100, as their squared correlation coefficients to axis 2 were low (0.08 and 0.01, respectively). These results were consistent with those of the Duncan tests, showing that fruity attributes decreased because they were masked by these powerful notes.

PCAs carried out after glass swirling (second perception) for Syrah wines (**Figure 6**) and Grenache wines (**Figure 7**) showed a different effect. All wines spiked with DMS clearly presented more complex aromatic profiles than their control wines. On the first axis, the attribute "fresh vegetable" was isolated, opposed to "jam" and "fruits in alcohol" for Grenache (**Figure 7A**) and to the group "jam", "fruits in alcohol", "dried fruits", "candied fruits", "garrigue", "pepper", and "black olive" for Syrah (**Figure 6A**). The attributes "truffle" and "undergrowth", which characterized the effect of DMS addition at first perception, were correlated at second perception to the second axis for both PCAs, and "black olive" was significantly correlated for the Grenache PCA only (**Figure 7A**). In addition, the fruity

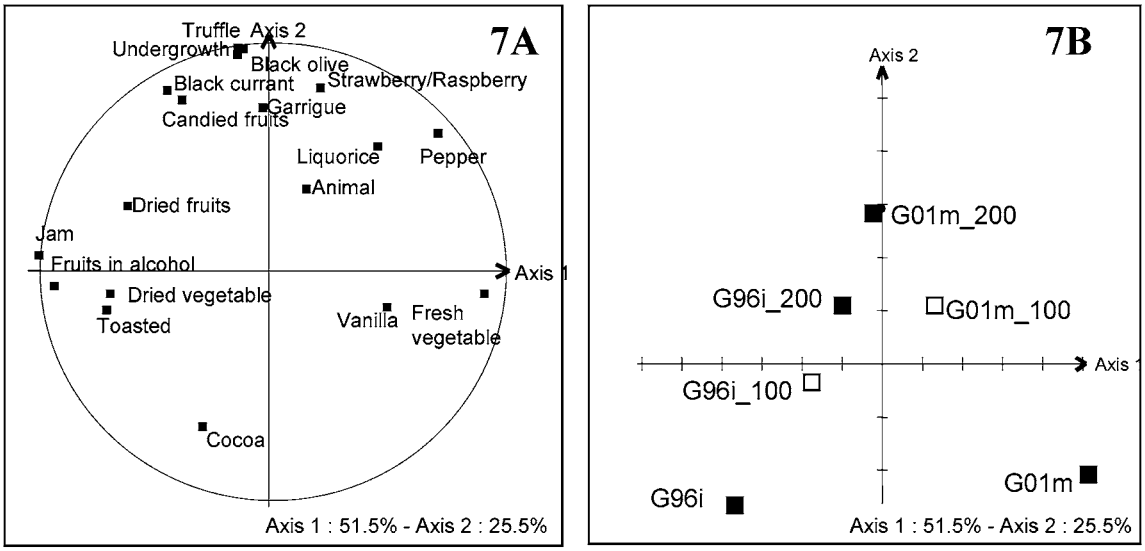

Figure 7. Projection of the Grenache Noir wines with and without DMS addition (**Table 1**) and sensory variables (**Table 3**) on the first two axes of the PCA carried out using the olfactory profiles at second perception (after glass swirling): (**A**) correlation circle; (**B**) projection of samples; (■) samples significantly represented on the first plane (sum of squared correlation coefficients on the two first axes higher than 0.5); (□) samples not significantly represented on the first plane (sum of squared correlation coefficients on the two first axes lower than 0.5).

attribute "black currant" was correlated to this second axis for both PCAs, and "strawberry/raspberry" was also significantly correlated for Grenache samples (**Figure 7A**). The projection of samples in the first plane (**Figures 6B** and **7B**) showed that the wines were mainly separated, on axis 1, by the vintage (except for sample S01d_200, as its squared correlation coefficient to this axis was 0.02), and, on axis 2, by DMS addition (except for samples G96i_100 and G01m100, as their squared correlation coefficients to this axis were 0.01 and 0.13, respectively), which showed that although DMS had a sensory effect, it did not mask each wine's aroma character. Higher DMS concentration tended to amplify these effects.

These results clearly demonstrated that DMS levels near 100 μg/L had a great impact on the aroma of the Grenache and the Syrah wines studied and that its effect was complex. DMS is one of the main constituents of truffle aroma (*41*, *42*), and truffle notes were previously reported as induced by DMS addition in oak barrel aged wines (*11*). The high volatility of DMS could explain why it may concentrate in the glass headspace and dominate the first olfactory perception. This concentration effect then presumably decreases with glass swirling. The DMS concentration, although tending to enhance the sensory effects, was never perceived as faulty by the panel. This result differed from observations by Spedding (*21*), who found that DMS degraded the quality of white wines at concentrations >60 μg/L and of a red Pinot wine when present at trace level. Anocibar Beloqui (*11*) also reported "green olive"-like notes appearing at DMS levels >100 μg/L in red wines. The effect of fruity notes enhancement (i.e., "fruits in alcohol", "jam", "black currant", "strawberry/raspberry", depending on the wine) was in agreement with previous observations in red wines (*11*, *19*), also emphasizing the high DMS levels (up to 4 mg/L) in liquors made with raspberry and black currant berries (*11*). Thus, it can be concluded from previous works and from our own results that the effect of DMS on wine aroma depended on the type of wine, that is, on interactions, whatever their nature, with specific flavor constituents, and on dynamic aroma release. Further disclosure of DMS flavor perception is needed for a deeper understanding of its impact on the aroma of wine.

ABBREVIATIONS USED

DMS, dimethyl sulfide; DMSO, dimethyl sulfoxide; SMM, *S*-methylmethionine; PDMS, potential dimethyl sulfide, as DMS released by heat−alkaline treatment; PCA, principal component analysis. GC-EIMS, gas chromatography−electron impact mass spectrometry; SPME, solid-phase microextraction; hL, hectoliter (100 L).

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