Vitis **26,** 79—84 (1987)

Department of Chemistry, University of Auckland, Auckland, New Zealand

Department of Scientific and Industrial Research, Division of Horticulture and Processing, Te Kauwhata Research Station, Te Kauwhata, New Zealand

Dimethyl sulphide in some Australian red wines

by

S. J. DE MORA[1]), S. J. KNOWLES[1]), R. ESCHENBRUCH[2]) and W. J. TORREY[3])

Dimethylsulfid in einigen australischen Rotweinen

Zusammenfassung: Es wird gezeigt, daß die DMS-Konzentrationen in Cabernet-Sauvignon-Weinen des Coonawarra-Distrikts in Südaustralien von 42 bis 910 $\mu g\ l^{-1}$ variierten. Die DMS-Mengen waren unabhängig vom Alter der Weine, sie variierten jedoch zwischen den Weinjahrgängen. Die Untersuchungen widerlegen nicht, daß DMS während der Flaschenreife entstehen kann, denn sie sind nur von einmaligem — „historischem" — Charakter. Die DMS-Gehalte scheinen jahrgangsabhängig und von Weinbau und Weinbereitung beeinflußt zu sein. Der Geruchsschwellenwert von DMS in Cabernet Sauvignon ist 0.07 $\mu l\ l^{-1}$ (60 $\mu g\ l^{-1}$).

Key words: red wine, sulphur, constituent, flavour, analysis, sensory rating, Australia.

Introduction

Volatile sulphur-containing compounds can contribute to the aroma and flavour of wine (SCHREIER 1979; NYKÄNEN and SUOMALAINEN 1983). Several different sulphur compounds have been identified and dimethyl sulphide (DMS) in particular has been suggested to have an influence on the bouquet of wines (DU PLESSIS and LOUBSER 1974; SIMPSON 1979). SPEDDING and RAUT (1982) demonstrated flavour improvement of Müller-Thurgau wines brought about by certain DMS levels. While too much DMS was considered faulty, low concentrations were found advantageous. In Australia, many red wines have characteristic aromas and flavours believed by some people to be typical and desirable, others, however, consider these to represent off-character. DMS could cause such marked differences of opinion.

A number of 'historical' surveys of wines have been conducted in which wines from several vintages are all analysed at one time. Some such studies have observed an increase in DMS concentrations with vintage age (LOUBSER and DU PLESSIS 1976; SIMPSON 1979), while other workers have found no trend (SPEDDING *et al.* 1980 and 1983). Historical surveys by their very nature cannot provide definitive evidence for DMS formation during bottle ageing. In examining white wines from a single vintage through a 16 week period, MARAIS (1979) did find that DMS levels rose with an increase in storage time or temperature.

DMS in red wine has been documented for some European wines (LEPPÄNEN *et al.* 1980) and some New Zealand wines (SPEDDING *et al.* 1980). In this study, red wines from

[1]) Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand.

[2]) Department of Scientific and Industrial Research, Division of Horticulture and Processing, Te Kauwhata Research Station, P.O. Box 19, Te Kauwhata, New Zealand.

[3]) Lindemans Wines Pty Ltd., Nyrang Cellars, 31 Nyrang Street, P. O. Box 19, Lidcombe 2141, N. S. W., Australia.

Cabernet Sauvignon grapes vintaged between 1966 and 1981 in the Coonawarra district of southeast South Australia have been analysed to determine DMS concentrations. In addition, a tasting panel determined the odour threshold of DMS in red wine.

Materials and methods

1. Wines

The wines analysed were made solely from Cabernet Sauvignon grapes grown in the Coonawarra district of southeast South Australia and all wines were made at the same Coonawarra winery. The wine used for the sensory evaluation trials was 1984 Cabernet Sauvignon sourced from a Victorian winery.

2. Analyses

Volatile sulphur compounds in wine were determined by headspace gas analysis (SPEDDING *et al.* 1980). Briefly, a bottle of wine was opened, a 100 cm^3 headspace created over 600 cm^3 of wine and then re-corked. Following equilibration for 12 h at 20 ± 1 °C, a sample of the headspace gas was removed for analysis. Using a 1 cm^3 sample loop and permeation pump, an aliquot was injected into the gas chromatograph (Pye Unicam PU 4500 equipped with a flame photometric detector). Sulphur volatiles were separated isothermally at 50 °C using a teflon column (2 m × 0.25 mm) packed with Carbopack B/1.5 % × XE60/1 % H_3PO_4 (Supelco Inc.). The following gases were quantified using permeation tubes: H_2S, SO_2, CH_3SH, CS_2 and DMS (O'KEEFFE and ORTMAN 1966).

Sulphur volatile concentrations have been determined in the headspace above the wine. These are related to the concentration within the wine itself via the partition coefficient, K_i, which is defined as:

$$K_i = \frac{C_i\,(g)}{C_i\,(l)}$$

where C_i (g) is the concentration component i in the headspace gas and C_i (l) is the liquid phase concentration of component i.

Due to the paucity of data for partition coefficients, those for DMS and CS_2 were estimated using the standard additions method. That is, an exact amount of analyte was added to a known volume of liquid beneath a known headspace volume. Following equilibration, the concentration in the headspace was determined as described previously. Partition coefficients may vary with temperature, ionic strength and analyte concentration. The partition coefficients for DMS and CS_2 were determined for different liquid phases, namely distilled water, grape juice, wine and a synthetic mineral medium prepared as per TOKUYAMA *et al.* (1973). A range of temperatures and analyte concentrations was investigated for the partitioning from distilled water and grape juice.

3. Sensory evaluation

The odour threshold for DMS was determined in a Cabernet Sauvignon wine with no detectable DMS by a taste panel consisting of wine industry personnel experienced in wine tasting. Each was presented with triangular tests and required to identify by the aroma the odd sample and state whether it had more or less DMS. Significance levels of the responses to the triangular tests were determined according to MINOZA-GATCHALIAN (1981).

The DMS used in these trials was obtained from Tokyo Kasei Kogyo Co., Ltd. (Guaranteed Reagent, Lot FATO3).

Results and discussion

Partition coefficients for DMS and CS_2 are presented in Table 1. Although relatively few partition coefficients for DMS are available for comparative purposes, the following values are calculated from PRZYJAZNY *et al.* (1983) for different DMS concentrations in distilled water at 21 °C: 0.061 (10,000 µg l^{-1}), 0.063 (1,000 µg l^{-1}) and 0.059 (100 µg l^{-1}). Our values for DMS in distilled water are somewhat lower: 0.046 (2120 µg l^{-1}), 0.044 (424 µg l^{-1}) and 0.044 (85 µg l^{-1}). In both studies there is no consistent relationship between analyte concentration and the partition coefficient. The influence of the DMS concentration is minor, especially in relation to the temperature effect observed.

The partition coefficient for DMS from wine (0.041) is slightly lower than that observed from distilled water under similar conditions (0.044). SPEDDING *et al.* (1980) cite a value of 0.43 for DMS from wine which must be considered to be an overestimate.

The only sulphur gas detected in the Cabernet Sauvignon wines from Coonawarra was DMS. Concentrations are given in Table 2. The first column gives the quantity

Table 1

Partition coefficients for DMS and CS_2 under various conditions

Verteilungskoeffizienten für DMS und CS_2 unter verschiedenen Bedingungen

Compound	Liquid phase	Temperature (°C)	Analyte concentration (nl l^{-1})	Partition coefficient
DMS	Distilled water	15	2 500	0.033
		21	2 500	0.046
		30	2 500	0.055
		21	500	0.044
		21	100	0.044
	Grape juice	15	500	0.056
		21	500	0.070
		30	500	0.086
	Mineral medium	21	500	0.049
	Wine	21	500	0.041
CS_2	Distilled water	15	500	0.023
		21	500	0.028
		30	500	0.037
	Grape juice	15	100	0.015
		21	100	0.024
		30	100	0.026
	Mineral medium	21	100	0.023
	Wine	21	100	0.016

Table 2

DMS concentrations in some Cabernet Sauvignon wines from the Coonawarra district

DMS-Konzentrationen einiger Cabernet-Sauvignon-Weine aus dem Coonawarra-Gebiet

Year	Identification no.	a) DMS $nl\,l^{-1}$ (g)	b) DMS $nl\,l^{-1}$ (l)	c) DMS $\mu g\,l^{-1}$ (l)
1966	3563	2	49	42
1970	4023	3	73	62
1975	5160	10	244	207
1977	5560	4	98	83
1978	5760	19	463	393
1979	5860	17	417	354
1980	5960	44	1 073	910
1981	6260	4	98	83
1981	6261	8	195	165

a) Headspace concentration.
b) Liquid phase concentration was estimated using partition coefficient 0.041.
c) Based on density of DMS at 20 °C equal to 0.848 (WEAST 1979).

actually measured in the headspace gas while the second and third columns give the calculated concentration in the wine itself. The DMS concentrations varied in the range 42—910 $\mu g\,l^{-1}$. These values are high, as expected from the known character of the wine, but generally they fall within the range of concentrations which have been observed in wine: 0—74 $\mu g\,l^{-1}$ (SPEDDING *et al.* 1980), 0—86 $\mu g\,l^{-1}$ (MARAIS, 1979), 20—117 $\mu g\,l^{-1}$ (SIMPSON 1979), 0—474 $\mu g\,l^{-1}$ (LOUBSER and DU PLESSIS 1976). The exception to this observation is the maximum value, 910 $\mu g\,l^{-1}$ for the 1980 Cabernet Sauvignon, which is higher than any previously reported DMS concentration. The considerable variation in DMS levels in the Coonawarra wines may account for the opposing views of acceptance and perception of many Australian red wines.

It is important to emphasize that there is no consistent trend in the DMS concentration as a function of age. Levels vary from vintage to vintage in agreement with the observations of SPEDDING *et al.* (1980 and 1983). The work of MARAIS (1979) does indicate that DMS levels may rise during bottle-ageing. However, initial DMS concentrations may be quite different from one year to the next depending upon the composition of the fruit. Additionally, the influence of winemaking practices should not be underestimated. DMS evolution is initiated by the onset of fermentation of grape juice (ESCHENBRUCH *et al.* 1986). Overzealous reductive vinification using a susceptible juice composition may enhance the generation of DMS. The wine yeast *Saccharomyces cerevisiae* can produce DMS (DE MORA *et al.* 1986), particularly during prolonged contact between the wine and lees. Cysteine was shown to be a DMS-precursor in this case, possibly accounting for the relative importance of fruit composition. Because the initial DMS level is dependent upon the vintage and winery, historical surveys of wines will only exhibit a trend of increasing DMS concentrations if two conditions are met. Firstly, the amount of DMS initially present must be low relative to that subsequently produced in the bottle in order that initial variations become masked. Secondly, the rate of DMS evolution must be comparable for all vintages. The results for this Australian Cabernet Sauvignon suggest that this first condition is not met.

Sensory evaluation results are presented in Table 3. DMS can be detected (odour perception) with significance of 0.5 % at a level of 0.07 $\mu l\,l^{-1}$ (or 60 $\mu g\,l^{-1}$). While this is

Table 3

Level of odour perception of DMS in Cabernet Sauvignon 1984 by the triangle test

Schwellenwerte von DMS in Cabernet Sauvignon 1984, bestimmt mit dem Dreieckstest

Taster no.	DMS added ($\mu l\ l^{-1}$)				
	0.10	0.07	0.04	0.02	0.01
1	1	1	0	1	1
2	1	1	0	0	0
3	1	1	1	1	1
4	1	1	1	0	1
5	1	1	0	1	0
6	0	1	1	1	0
7	1	1	0	0	0
8	1	0	0	0	0
9	1	0	0	0	0
10	1	1	0	0	0
Total correct responses	9	8	3	4	3
Significance levels	0.1 %	0.5 %	NS	NS	NS

Key: 1 = Correct response.
0 = Incorrect response.
NS = Not significant at 5 %.

higher than that reported for white wine (0.03 $\mu l\ l^{-1}$ or 25 $\mu g\ l^{-1}$) DMS (Spedding and Raut 1982), the result is not unexpected as Cabernet Sauvignon wines generally have a more complex and mouth-filling character (whether from the fruit or oak) than a fresh and fruity Riesling × Sylvaner. It is noted that individuals have different capabilities in relation to detection of sulphur compounds, with some wine industry personnel being extremely sensitive.

Different wines will also vary in respect to their capacity to tolerate the presence of DMS, depending on the intensity of character in the wine concerned. Spedding and Raut (1982) suggested that Gewürztraminer, being a very fruity and floral wine, was probably more tolerant to added DMS. Of the wines tested, the presence of DMS was very obvious in the 1980 Coonawarra Cabernet Sauvignon. However, the majority of tasters did not consider the level objectionable because of the complexity and depth of character in the wine. It was also observed that the DMS character was an integral part of the bouquet and did not appear out of place or disjointed. In the tasting trials low levels of DMS were found to enhance the fruit character of the control wine.

Summary

DMS levels in Cabernet Sauvignon wine from the Coonawarra area of southeast South Australia were shown to vary from 42 to 910 $\mu g\ l^{-1}$. Results indicate that the levels are not dependent on age but rather vary from vintage to vintage. This study does not discount the development of DMS with bottle age as it is an 'historical' survey but

suggests that the levels of DMS are vintage related and may depend on viticultural practices and vinification techniques. The odour threshold for DMS in Cabernet Sauvignon was 0.07 μl l^{-1} (60 μg l^{-1}).

References

1. DE MORA, S. J.; ESCHENBRUCH, R.; KNOWLES, S. J.; SPEDDING (the late), D. J.; 1986: The formation of dimethyl sulphide during fermentation using a wine yeast. Food Microbiol. **3**, 27—32.
2. DU PLESSIS, C. S.; LOUBSER, G. J.; 1974: The bouquet of 'late harvest' wine. Agrochemophysica **6**, 49—52.
3. ESCHENBRUCH, R.; DE MORA, S. J.; KNOWLES, S. J.; LEONARD, W. K.; FORRESTER, T.; SPEDDING (the late), D. J.; 1986: The formation of volatile sulphur compounds in unclarified grape juice. Vitis **25**, 53—57.
4. LEPPÄNEN, O. A.; DENSLOW, J.; RONKAINEN, P. P.; 1980: Determination of thiolacetates and some other volatile sulphur compounds in alcoholic beverages. J. Agricult. Food Chem. **28**, 359—362.
5. LOUBSER, G. J.; DU PLESSIS, C. S.; 1976: The quantitative determination and some values of dimethyl sulphide in white table wines. Vitis **15**, 248—252.
6. MARAIS, J.; 1979: Effect of storage time and temperature on the formation of dimethyl sulphide and on white wine quality. Vitis **18**, 254—260.
7. MINOZA-GATCHALIAN, M.; 1981: Sensory Evaluation Methods with Statistical Analysis. College of Home Economics, University of the Philippines, Diliman, Quezon City, Philippines.
8. NYKÄNEN, L.; SUOMALAINEN, H.; 1983: Aroma of Beer, Wine and Alcoholic Beverages. D. Reidel Publishing Co., Dordrecht, Holland.
9. O'KEEFE, A. E.; ORTMAN, G. C.; 1966: Primary standards for trace gas analysis. Analyt. Chem. **38**, 760—763.
10. PRZYJAZNY, A.; JANICKI, W.; CHRZANOWSKI, W.; STASZEWSKI, R.; 1983: Headspace gas chromatographic determination of distribution coefficients of selected organosulphur compounds and their dependence on some parameters. J. Chromatogr. **280**, 249—260.
11. SCHREIER, P.; 1979: Flavour composition of wines: A review. CRC Crit. Rev. Food Sci. Nutr. **12**, 59—111.
12. SIMPSON, R. F.; 1979: Aroma composition of bottle aged white wine. Vitis **18**, 148—154.
13. SPEDDING, D. J.; ESCHENBRUCH, R.; MCGREGOR, P. J.; 1983: Sulphur compounds in the headspace of some New Zealand commercial wines. Food Technol. Austral. **35**, 22—23.
14. — —; ESCHENBRUCH, R.; PURDIE, A.; 1980: The distribution of dimethyl sulphide in some New Zealand wines. Vitis **19**, 241—245.
15. — —; RAUT, P.; 1982: The influence of dimethyl sulphide and carbon disulphide in the bouquet of wines. Vitis **21**, 240—246.
16. TOKUYAMA, T.; KURAISHI, H.; AIDA, K.; UEMARA, T.; 1973: Hydrogen sulphide evolution due to pantothenic acid deficiency in the yeast requiring this vitamin with special reference to the effect of adenosine triphosphate on yeast cysteine desulphydrase. J. Gen. Appl. Microbiol. **19**, 439—466.
17. WEAST, R. (Ed.); 1979: CRC Handbook of Chemistry and Physics, CRC Press, Inc., West Palm Beach.

Eingegangen am 18. 6. 1986

Dr. S. J. DE MORA
Department of Chemistry
University of Auckland
Private Bag
Auckland
New Zealand