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The influence of dimethyl sulphide and carbon disulphide in the bouquet of wines

by

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Der Einfluß von Dimethylsulfid und Schwefelkohlenstoff auf das Weinaroma

Zusammenfassung. — Bei der sensorischen Beurteilung von Weinen, denen Dimethylsulfid in sehr niedrigen Konzentrationen zugesetzt worden war, wurden jene mit $0,022 \mu\text{l} \cdot \text{l}^{-1}$ vor solchen ohne oder mit $0,044 \mu\text{l} \cdot \text{l}^{-1}$ Dimethylsulfid bevorzugt. Geringe DMS-Mengen können demnach die Weinqualität positiv beeinflussen.

Die sensorisch wahrnehmbare Schwefelkohlenstoffkonzentration war höher als die in den Weinen gefundenen Mengen.

Der Geruchsschwellenwert für Dimethylsulfid in Aqua dest. betrug $7,5 \times 10^{-5} \mu\text{l} \cdot \text{l}^{-1}$, der Geschmacksschwellenwert dagegen $4 \times 10^{-4} \mu\text{l} \cdot \text{l}^{-1}$.

Introduction

Dimethyl sulphide (DMS) has been detected in the headspace of a number of white wines (DU PLESSIS and LOUBSER 1974, LOUBSER and DU PLESSIS 1976, SIMPSON 1979, MARAIS 1979, LEPPÄNEN *et al.* 1980, SPEDDING *et al.* 1980) and to a lesser extent in red wines (LEPPÄNEN *et al.* 1980, SPEDDING *et al.* 1980). The concentrations ranged from 0 to $0.402 \mu\text{l} \cdot \text{l}^{-1}$ with most being less than $0.1 \mu\text{l} \cdot \text{l}^{-1}$. Carbon disulphide (CS_2) has also been reported in wines (LEPPÄNEN *et al.* 1980, SPEDDING *et al.*, submitted) at concentrations ranging from 0 to $0.013 \mu\text{l} \cdot \text{l}^{-1}$.

Sensory evaluations on wines containing DMS suggest that this compound contributes to the overall aroma (DU PLESSIS and LOUBSER 1974, SIMPSON 1979), particularly to the maturation bouquet (MARAIS 1979). It is of interest to note that the Council of Europe includes DMS up to a level of 1.4 ppm ($1.35 \mu\text{l} \cdot \text{l}^{-1}$) in a list of artificial flavouring substances that may be added to foodstuffs without hazard to public health (COUNCIL OF EUROPE 1974).

It is the objective of this paper to determine those concentrations of DMS and CS_2 that represent their level of perception in a white and red wine, and also to assess their influence on wine quality. In addition, the tasting panel was used to determine a threshold value for the taste and smell of DMS in distilled water.

Materials and methods

1. Selection of tasting panel

20 volunteers from the Department of Chemistry, University of Auckland, were screened for their ability to:

- (a) discriminate sweetness with a range of 7 dilute aqueous sucrose solutions ($0-40 \text{ g} \cdot \text{l}^{-1}$);

- (b) discriminate acidity with a range of 7 dilute aqueous citric acid solutions (0—0.5 g · l⁻¹);
- (c) discriminate odours by smelling dilute solution of geraniol, limonene, terpineol, β-pinene, and acetaldehyde;
- (d) discriminate the presence of DMS in white wine in 5 duo-trio tests (AMERINE and ROESSLER 1976).

This experiment provided a panel of 9 tasters.

2. Wines

The wines were from the experimental production of the Te Kauwhata Viticultural Research Station, New Zealand. None of the panel had previous access to these wines. Wines used were: for panel selection, level of perception, and difference in quality — Riesling × Sylvaner 1981; and for difference in quality only — Riesling × Sylvaner 1980, Pinot Chardonnay 1980, Gewürztraminer 1977, Pinot noir 1978. All samples were analysed for DMS and CS₂ by headspace analysis using a sulphur gas analyser as previously described (SPEDDING *et al.* 1980).

Table 1

Scorecard for difference in quality determination (MARIE *et al.* 1962)
 Beurteilungsschema zur Ermittlung von Qualitätsunterschieden (MARIE *et al.* 1962)

| Characteristic | Weighting | Multiplying factor |
|--------------------|-----------|---|
| Odour intensity | 1 | Strong (× 3), medium (× 2), weak (× 1) |
| Taste intensity | 2 | Strong (× 3), medium (× 2), weak (× 1) |
| Odour quality | 2 | Outstanding (× 3), very good (× 2), good (× 1), acceptable (× 0), unacceptable (× -1) |
| Taste quality | 3 | Outstanding (× 3), very good (× 2), good (× 1), acceptable (× 0), unacceptable (× -1) |
| General impression | 2 | Excellent (× 3), very good (× 2), good (× 1), fair (× 0), poor (× -1), very poor (× -2), extremely poor (× -3). |

3. Sensory evaluation

Tasting experiments were conducted once a week in a large seminar room between 9 a. m. and 11 a. m. Each sample was presented to the panel in a different glass (covered in the case of odour evaluation). Communication between judges was impossible. All bottles were wrapped in a similar paper and were uncorked in the presence of the panel (sulphur compounds were added to the samples 2 h before tasting and the bottles were recorked).

For the selection of the panel and for the tests of level of perception, standard questionnaires were used, i. e. ranking, duo-trio, triangle test (AMERINE and ROESSLER 1976). The questionnaire used to determine the difference in quality was based on the scoreboard of the Office International de la Vigne et du Vin, Paris (MARIE *et al.* 1962) and is outlined in Table 1.

All results were subjected to the analysis of variance. In the test on difference in quality the following total (T) was used for each wine:

$$T = (\text{Odour intensity} \times 2 \text{ odour quality}) + (2 \text{ taste intensity} \times 3 \text{ taste quality}) + (2 \text{ general impression})$$

In order to determine the DMS thresholds of taste and smell in distilled water the following concentrations of DMS were used: for odour threshold — $0, 9.4 \times 10^{-6}, 1.9 \times 10^{-5}, 3.8 \times 10^{-5}, 7.5 \times 10^{-5}, 1.5 \times 10^{-4}, 3 \times 10^{-4}, 6 \times 10^{-4} \mu\text{l} \cdot \text{l}^{-1}$. The samples were presented in covered glasses. For taste threshold — $1 \times 10^{-5}, 2 \times 10^{-5}, 1 \times 10^{-4}, 2 \times 10^{-4}, 4 \times 10^{-4}, 2 \times 10^{-3}, 4 \times 10^{-3}, 9 \times 10^{-3} \mu\text{l} \cdot \text{l}^{-1}$. These samples were presented in squeeze bottles to avoid influences on the sense of smell. In determining the threshold the panel were required to rank the samples in which they could detect DMS. A mark of 7 was given to the strongest detection with decreasing marks until non-detection was reached where a mark of 0 was given. The order of presentation of the samples was different for each judge and was chosen at random.

Table 2
Dimethyl sulphide concentrations in wines used for tasting
Dimethylsulfidkonzentration der zur Verkostung angestellten Weine

| Wine | DMS concentration ($\mu\text{l} \cdot \text{l}^{-1}$) |
|---------------------------------|---|
| Riesling \times Sylvaner 1981 | 0.008 |
| Riesling \times Sylvaner 1980 | 0.012 |
| Gewürztraminer 1977 | 0.015 |
| Pinot Chardonnay 1980 | 0.015 |
| Pinot noir 1978 | 0.013 |

Results and Discussion

1. Selection of panel

The 9 tasters selected for the panel made no mistake in sweetness and acidity discrimination, made a maximum of 1 mistake in the 5 duo-trio wine tests, and recognised a minimum of 4 odours out of 9.

2. Sulphur gas analysis of wines

The results of the analysis are set out in Table 2. It can be seen that there is a close similarity in DMS levels in all but the Riesling \times Sylvaner 1981 which had about half the DMS concentration of the other wines. This difference was considered in tests involving the addition of DMS.

3. Sensory evaluation

Table 3 lists the results of a triangle test for the taste and odour perception of DMS and CS₂. Each judge was presented with 5 samples containing $0.03 \mu\text{l} \cdot \text{l}^{-1}$ DMS, $0.06 \mu\text{l} \cdot \text{l}^{-1}$ DMS, $0.09 \mu\text{l} \cdot \text{l}^{-1}$ DMS, $0.01 \mu\text{l} \cdot \text{l}^{-1}$ CS₂ and $0.03 \mu\text{l} \cdot \text{l}^{-1}$ CS₂.

Table 3

Level of perception of DMS and CS₂ in Riesling × Sylvaner 1981 by the triangle test
 Nachweisgrenze für DMS und CS₂ bei Riesling × Sylvaner 1981 bei Anwendung des Dreieckstests

| Judge no. | Sulphur compounds added ($\mu\text{l} \cdot \text{l}^{-1}$) | | | | |
|-----------------------|---|----------|----------|----------------------|----------------------|
| | 0.09 DMS | 0.06 DMS | 0.03 DMS | 0.03 CS ₂ | 0.01 CS ₂ |
| 1 | 1 | 1 | 0 | 1 | 0 |
| 2 | 1 | 1 | 1 | 0 | 0 |
| 3 | 1 | 1 | 1 | 0 | 0 |
| 4 | 1 | 1 | 1 | 0 | 0 |
| 5 | 1 | 1 | 1 | 0 | 0 |
| 6 | 0 | 1 | 1 | 0 | 0 |
| 7 | 1 | 0 | 1 | 0 | 0 |
| 8 | 1 | 0 | 1 | 0 | 0 |
| 9 | 0 | 0 | 1 | 0 | 0 |
| Level of significance | 0.1 % | 0.1 % | 0.1 % | NS | NS |

1 = Correct response.

0 = Wrong response.

NS = Not significant.

Table 4

Flavour ranking test on 1981 Riesling × Sylvaner with varying concentrations of added DMS
 Rangordnung bei der Aromabeurteilung von Riesling × Sylvaner 1981 mit unterschiedlichem DMS-Zusatz

| Concentration of DMS added ($\mu\text{l} \cdot \text{l}^{-1}$) | Rank mean from all judges |
|---|---------------------------|
| 0 | 0.742 |
| 0.02 | 0.898 |
| 0.03 | 0.183 |
| 0.04 | -0.018 |
| 0.06 | -0.292 |
| 0.09 | -0.658 |
| 0.15 | -0.848 |

F = 10.36 (level of significance 1 ‰).

LSD 1 ‰ = 1.

As little as 0.03 $\mu\text{l} \cdot \text{l}^{-1}$ DMS was detected at a significance level of 0.1 %. The panel should thus be able to be used to give information on the quality of the difference between wine with and without added DMS. On the other hand, the panel could not determine the difference between a blank and the same wine with an addition of 0.03 $\mu\text{l} \cdot \text{l}^{-1}$ CS₂. This concentration is greater than that found in any commercial wine, hence the influence of CS₂ on wine bouquet was not further investigated.

Table 5

Mean values of T¹⁾ determining the difference in quality of wines with added DMS
Mittlere T-Werte¹⁾ zur Bestimmung von Qualitätsunterschieden bei Weinen mit DMS-Zusatz

| Wine | Amount of added DMS ($\mu\text{l} \cdot \text{l}^{-1}$) | | | Level of significance | LSD |
|---------------------------------|---|-------|-------|-----------------------|------|
| | 0 | 0.022 | 0.044 | | |
| Riesling \times Sylvaner 1981 | 10.9 | 25.6 | 10.9 | 5 % | 12 |
| Riesling \times Sylvaner 1980 | 9.8 | 20 | -8 | 1 % | 11.3 |
| Gewürztraminer 1977 | 8.7 | 18.7 | 11.9 | 5 % | 7.6 |
| Pinot Chardonnay 1980 | 7.3 | 13.3 | 2 | 5 % | 7.1 |
| Pinot noir 1978 | 26.1 | 18.1 | 16 | 5 % | 8 |

¹⁾ T is defined in the text.

Table 6

The determination of thresholds of taste and smell for DMS in distilled water
Die Bestimmung der Geschmacks- und Geruchsschwellenwerte von DMS in Aqua dest.

| Odour experiment | | | Taste experiment | | |
|---|----------------------|------------------|---|----------------------|------------------|
| DMS added ($\mu\text{l} \cdot \text{l}^{-1}$) | Mean mark (see text) | Group (see text) | DMS added ($\mu\text{l} \cdot \text{l}^{-1}$) | Mean mark (see text) | Group (see text) |
| 0 | 1.1 | 2 | 1×10^{-5} | 1 | 2 |
| 9.4×10^{-6} | 1.4 | 2 | 2×10^{-5} | 1.1 | 2 |
| 1.9×10^{-5} | 1.3 | 2 | 1×10^{-4} | 1.4 | 2 |
| 3.8×10^{-5} | 0.9 | 2 | 2×10^{-4} | 1.7 | 2 |
| 7.5×10^{-5} | 4.2 | 1 | 4×10^{-4} | 3.2 | $\frac{1}{2}$ |
| 1.5×10^{-4} | 3.8 | 1 | 2×10^{-3} | 4.5 | 1 |
| 3×10^{-4} | 5.7 | 1 | 4×10^{-3} | 5.7 | 1 |
| 6×10^{-4} | 4.8 | 1 | 8×10^{-3} | 6.1 | 1 |

In an experiment to rank a wine according to flavour, the panel was presented with 7 glasses of wine with additions of 0, 0.02, 0.03, 0.04, 0.06, 0.09 and $0.15 \mu\text{l} \cdot \text{l}^{-1}$ DMS. The results of this experiment are outlined in Table 4. All but the first 2 samples were placed in the ranking order of their concentrations. The least significant difference suggests that the limit of acceptability probably lies between 0.04 and $0.06 \mu\text{l} \cdot \text{l}^{-1}$ added DMS. (Reaction of the panel during the experiment also supports this result.)

The difference in quality of a number of wines with and without the addition of DMS was determined using the T value (see Table 5). The result for the only red wine, Pinot noir, was different from the others. The panel preferred this wine without DMS. This may have been due to the fact that the wine was full-bodied with a rich bouquet. In the case of the white wines, on all occasions the panel mean showed a preference for an addition of $0.022 \mu\text{l} \cdot \text{l}^{-1}$ DMS, at a level of significance of 5 % and LSD 9.5 (Table 5). Except for the Gewürztraminer, wines with $0.044 \mu\text{l} \cdot \text{l}^{-1}$ added DMS were statistically less favoured than those with $0.022 \mu\text{l} \cdot \text{l}^{-1}$ DMS. The Gewürztraminer was a very fruity wine and, therefore, was probably more tolerant to added DMS. If the data for all of the

white wines in Table 5 are taken together, the overall mean values for T are 9.2, 19.4 and 4.2 for 0, 0.022 and 0.044 $\mu\text{l} \cdot \text{l}^{-1}$ added DMS, respectively.

The determination of the thresholds of taste and smell for DMS in distilled water is outlined in Table 6. The analysis of variance for the odour threshold is $F = 6.30$ (significant at 0.1 %) and $\text{LSD at } 5\% = 1.94$. This separated the results into two groups (labelled 1 and 2 in Table 6). The odour threshold may be considered to be the lowest value in group 1, i. e. $7.5 \times 10^{-5} \mu\text{l} \cdot \text{l}^{-1}$ (0.08 ppb) for DMS in distilled water. Reported values are 12 ppb (PATTON *et al.* 1956), 9 ppb (TOAN *et al.* 1965) and 0.33 ppb (GUADAGNI *et al.* 1963). It can be seen that the threshold obtained in this study is a factor of 4 below that established by GUADAGNI *et al.* (1963). However, Table 6 shows clearly that the panel could readily differentiate between DMS at $7.5 \times 10^{-5} \mu\text{l} \cdot \text{l}^{-1}$ and $3.8 \times 10^{-5} \mu\text{l} \cdot \text{l}^{-1}$, only a factor of 2 different in concentration.

The analysis of variance for the taste threshold is $F = 11.01$ (significant at 0.1 %) and $\text{LSD at } 5\% = 1.79$. Again, two groups become apparent (Table 6) identifying the taste threshold value as $4 \times 10^{-4} \mu\text{l} \cdot \text{l}^{-1}$ (0.44 ppb).

Summary

Sensory evaluation of DMS added to wines at very low concentrations has shown that addition of $0.022 \mu\text{l} \cdot \text{l}^{-1}$ resulted in statistically more favoured wines than those with no, or $0.044 \mu\text{l} \cdot \text{l}^{-1}$ added DMS. This shows that low concentrations of DMS can have a beneficial effect on the quality of some wines.

The concentration of CS_2 necessary to give any sensory response was higher than that observed in any commercial wine.

The threshold of smell for DMS in distilled water was found to be $7.5 \times 10^{-5} \mu\text{l} \cdot \text{l}^{-1}$ (0.08 ppb) while that for taste was $4 \times 10^{-4} \mu\text{l} \cdot \text{l}^{-1}$ (0.4 ppb).

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