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The distribution of dimethyl sulphide in some New Zealand wines

by

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Über das Vorkommen von Dimethylsulfid in einigen neuseeländischen Weinen

Zusammenfassung. — Von allen auf das Vorkommen von Dimethylsulfid (DMS) untersuchten neuseeländischen weißen und roten Versuchsweinen der Jahrgänge 1975—1980 zeigte zumindest ein Jahrgang die Anwesenheit dieser Aromakomponente. Ältere Weine scheinen ganz allgemein häufiger DMS zu enthalten als junge. Es wird vermutet, daß die hohe Streubreite von der Weinbereitung abhängt. Dimethylsulfoxid scheint die Vorstufe von DMS zu sein, das während des Alterungsprozesses auf der Flasche entstehen könnte.

In einigen Mosten wurde Carbonylsulfid nachgewiesen, das jedoch wegen seiner hohen Flüchtigkeit mit dem Gärgas entweichen dürfte.

Introduction

The importance of dimethyl sulphide (DMS) as a contributor to the bouquet of wines was first established by DU PLESSIS and LOUBSER (6). Subsequently DMS has been found in a range of white wines from South Africa (9, 11) and in white table wines from *Vitis vinifera* cv. Riesling grapes from Australia (13). Concentrations of DMS extending from 0 to 474 $\mu\text{g/l}$ have been found, with strong evidence that DMS developed in the bottle by aging processes (9, 11, 13) to become an important part of bottle age bouquet. In addition to storage time, it has been shown that storage temperature influences DMS concentration in bottled wine, with increasing temperature producing increasing DMS concentrations (11).

There have been many investigations into DMS in beers (see GARZO-ULLOA (8) for review) and it has been recognised that DMS is a normal component of beer flavour, having an important contribution to the flavour of lager beers. The origin of DMS in beers appears to be the malting process (8) and pathways for the formation and loss of the compound during the manufacture of beer have been established (8). The studies of the origin of DMS in beers by WAINWRIGHT and co-workers (2, 15) have provided a potential explanation for the development of DMS in bottle-aged wines. They have found that dimethyl sulphoxide may be produced by the oxidation of DMS and subsequently reduced to DMS by yeast cell suspensions and by cell-free extracts of yeast (2). The latter reduction process could be that which produces DMS in bottled wines.

DMS has been used industrially since the 1930's as a fragrance in soaps, detergents, creams, lotions, and perfumes (12). The Council of Europa (4) included DMS, up to a level of 1.5 ppm, in a list of artificial flavouring substances that may be ad-

ded to foodstuffs without hazard to public health. SIMPSON (12) has listed the flavour threshold values for DMS to range between 10 and 60 $\mu\text{g/l}$, very much below the suggested hazard level. At high concentrations the odour is repulsive and cabbage-like, while at very high dilution it becomes almost acceptable with a vegetable-like smell (3).

This paper reports the distribution of DMS amongst a number of experimental New Zealand wines, both white and red, from the years 1975 to 1980.

Materials and methods

1. Wines

The grapes from which the wines derived were from experimental vines at the Te Kauwhata Viticultural Research Station, North Island, New Zealand. All experimental wines were prepared according to the standard conditions outlined by ESCHENBRUCH and SAGE (7). The bottled wines were stored in bins exposed to temperature fluctuations between 10 and 20 $^{\circ}\text{C}$.

2. Analysis

A headspace of 100 ml was created above each 600 ml wine sample and this was analysed using a TRACOR model 270 HA sulphur gas analyser modified to separate the sulphur gases on a Porapak QS column as described by DE SOUZA *et al.* (5). The sulphur gas analyser was calibrated using a permeation tube containing authentic DMS. The emission rate of the permeation tube was determined by daily weighing to be 19.6 $\mu\text{g/l}$ DMS at 20 ± 1 $^{\circ}\text{C}$.

As previous DMS analyses in wine have been quoted as μg DMS/l of wine, the HENRY'S law relationship between solution DMS and headspace DMS was determined following addition of known volumes of DMS to wine samples maintained under the same conditions as those used for all DMS headspace analyses. The distribution coefficient of DMS between headspace and wine was found to be 0.43 which may be compared to a value of 0.30 for the distribution of DMS between air and seawater (10). The former value has been used in all work quoted in this paper to convert headspace concentration to an aqueous phase concentration.

Results and discussion

The results of the determination for DMS in New Zealand experimental wines are set out in Table 1, while those for juices are in Table 2. In addition to DMS the following sulphur gases were found in the headspace of the wines: sulphur dioxide, methyl mercaptan, dimethyl disulphide and two other unidentified compounds. Carbonyl sulphide (COS) was also identified in the headspace above some grape juices.

Table 1 shows that DMS is apparently randomly distributed amongst the wines tested. The data include the first report of DMS in red wines. An obvious trend in the data is the low incidence of DMS in young wines as compared to those of older vintages, with none being found as yet in any of the 1980 wines. These results follow those of MARAIS (11) who found DMS in only one of the wines tested that had been stored at 10 $^{\circ}\text{C}$, and that was found after 16 weeks storage. At

20 °C storage temperature DMS developed in as little as 3 weeks in the wines of MARAIS (11). Australian commercial Riesling wines showed DMS in each vintage year tested with the concentration rising from 28 µg/ml in 1977 to 117 µg/ml in 1967 (13). The variation seen in the present results may be due to the production of small quantities of wine for experimental purposes where the surface area to volume ratio is quite high and hence the potential for loss of DMS to the air is high. Experiment showed that within 1 h the DMS concentration in the 100 ml headspace above 600 ml of wine rose from zero to a constant value. The transfer of DMS from wine to air is thus a rapid process. It is intended to extend this work with a comprehensive survey of commercial wines produced in large quantity in New Zealand.

Two of the wines tested (Pinotage and Gamay Beaujolais) had been derived from grape juice that had been heated to 70 °C in order to extract more colour. It can be seen that in both cases heat extraction has increased the concentration of DMS above that of the wine from the untreated grape juice.

Analyses for DMS in grape juices (Table 2) were carried out in an attempt to determine whether or not the juices were a direct source of DMS in the resulting wine. The most important result is the presence of DMS in Riesling × Sylvaner juice. It can be seen from Table 1 that the wine derived from this juice had no measureable DMS. In beer manufacture, DMS losses by evaporation occur at a number of steps in the process (8). Similar losses are also possible in winemaking. The reappearance of DMS after bottle storage could be the result of reduction of dimethyl sulphoxide which is of much lower volatility than DMS. Further work is necessary in order to test this hypothesis.

The presence of COS in some juice samples is of interest. DMS is often found in tidal and marshy areas (see (1) for review) and this very recent report has shown

Table 1
DMS concentrations in New Zealand experimental wines
DMS-Konzentrationen neuseeländischer Versuchsweine

Variety	µg DMS/l wine					
	1975	1976	1977	1978	1979	1980
<i>Vitis vinifera</i> cvs.						
Riesling × Sylvaner	ND ²⁾	ND	38	ND	ND	ND
Gewürztraminer	1.6	22	17	1.6	ND	ND
Golden Chasselas	ND	ND	8.6	ND	ND	ND
Chardonnay	4.2	14	5.3	27	ND	ND
Pinotage	ND	4	4.4	17	0.5	—
Pinotage (HE 70 × 0) ¹⁾	7.2	17	8.4	36	—	—
Gamay Beaujolais	—	6.7	6.7	1.9	ND	ND
Gamay Beaujolais (HE 70 × 0) ¹⁾	—	16	8.1	1.4	—	—
Pinot Noir	—	74	ND	16	ND	ND
Cabernet Sauvignon	—	8.4	22	ND	ND	ND
French American Hybrids						
Baco 22 A	ND	11	21	ND	8.1	ND
Seibel 5437	—	5.1	3.3	7.2	3.0	—

¹⁾ HE (70 × 0) is heating the crushed fruit to 70 °C with 0 h holding time.

²⁾ ND is DMS concentration below sensitivity of detector.

Table 2

DMS concentrations in the juice of some New Zealand Grapes Vintage 1980
 DMS-Konzentrationen in einigen neuseeländischen Traubensäften, Lese 1980

Variety	µg DMS/l juice
<i>Vitis vinifera</i> cvs.	
Müller Thurgau	27
Riesling × Sylvaner	30
Gewürztraminer	ND ³⁾
24/125 ¹⁾	12 ⁴⁾
44/8 ¹⁾	7 ⁴⁾
Rabaner ²⁾	26 ⁴⁾
Reichensteiner ²⁾	32 ⁴⁾
4/46 ²⁾	ND ⁴⁾
Pinot Noir	ND
Gamay Beaujolais	ND
Cabernet Sauvignon	ND
French American hybrids	
Seibel 5437	ND
Seyve-Villard 20473	ND
Schuyler	12

¹⁾ New selection from Klosterneuburg, Austria.

²⁾ New selection from Geisenheim, Germany.

³⁾ ND is DMS concentration below sensitivity of detector.

⁴⁾ Carbonyl sulphide also formed.

that COS is simultaneously emitted from decaying vegetation in these areas. The sludge associated with juice samples represents a comparable situation being severely damaged vegetable matter in the first stages of decay. It is thus not surprising that COS was found in some juice samples. The absence of COS in wines is attributable to the physical properties of the compound which is a gas of boiling point -50°C . On the other hand, DMS is a liquid of boiling point 37.3°C (14). Any COS present in grape juice would doubtless be purged by carbon dioxide during fermentation.

Summary

All New Zealand experimental wines of the vintages 1975—1980 tested showed the presence of DMS in at least one vintage year, whether the wines were red or white. There was a general trend for older wines to have a higher probability for the presence of DMS than younger wines. The variability in the presence of DMS was suggested to be related to the processing of the wines. Dimethyl sulphoxide seems to be the precursor of DMS formed during bottle aging.

Carbonyl sulphide found in grape juices was thought to be lost during fermentation because of its high volatility.

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