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## The formation of volatile sulphur compounds in unclarified grape juice

by

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### Die Bildung flüchtiger Schwefelverbindungen in nicht-entschleimtem Traubensaft

**Zusammenfassung:** Die Entwicklung der flüchtigen Schwefelverbindungen Carbonylsulfid (OCS), Schwefelkohlenstoff (CS<sub>2</sub>) und Dimethylsulfid (DMS) während der Entschleimung frischer Müller-Thurgau- und Riesling-Moste wird beschrieben. Sofort nach dem Mahlen nahmen OCS und CS<sub>2</sub> zu. Höhere Temperaturen verstärkten diese Entwicklung. Mit Beginn der Gärung nahmen die Konzentrationen dieser Verbindungen ab. DMS wurde nur in gärenden Mosten gefunden.

**Key words:** must, fining, fermentation, temperature, sulphur, flavour.

### Introduction

The significance of volatile sulphur compounds contributing to the flavour of fresh fruit juices, e. g. tomatoes (CHUNG *et al.* 1983), citrus (SHAW and NAGY 1981) or kiwifruit (YOUNG and PATERSON, personal communication) is well recognised. Components like hydrogen sulphide (H<sub>2</sub>S), dimethyl sulphide (DMS) and carbonyl sulphide (OCS) have been identified as part of the aroma profile of these juices.

DMS and also OCS are often found in tidal and marshy areas, emitted from decaying vegetation (ANEJA *et al.* 1979). In a previous publication we reported the incidence of DMS and OCS in grape juices, which was considered to be caused by juice solids, severely damaged vegetable matter in the first stages of decay (SPEDDING *et al.* 1980). Since then we have shown the formation of DMS and methyl mercaptan by yeast during prolonged lees contact after fermentation (DE MORA *et al.*, in press).

In brewing, the importance of DMS and related compounds is slowly being unravelled (WILLIAMS and GRACEY 1982 a, b; DICKENSON 1983; BAMFORTH 1985), not so in wine-making. It is interesting to note that 'sulphur off-flavours' (other than H<sub>2</sub>S) are the subject of much concern and many discussions in German winemaking (WÜRDIG 1985). In this paper we report the formation of DMS, OCS and carbon disulphide (CS<sub>2</sub>) in freshly crushed, unclarified grape juice from 3 vintages.

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### Materials and methods

#### Grapes and sample preparation

During ripening of *Vitis vinifera* cvs. Müller-Thurgau and Riesling, both grown at the Te Kauwhata Research Station, grape samples were collected up to 4 times. The range of the most important juice parameters is presented in the table. After destemming and crushing of the grapes the juice was extracted with an experimental air-bag press (Willmes, 60 l capacity) at 4 atm pressure for 5 min. To half of the juice 80 mg of sodium metabisulphite/l was added. Then 200 ml of juice was poured into 250 ml graduated glass cylinders and stoppered in duplicate, leaving a headspace volume of 100 ml. Two sample lots with and without SO<sub>2</sub> addition were kept at 15 and 30 °C, respectively, providing 8 samples for headspace analysis of volatile sulphur components. Samples were allowed to equilibrate for 1 h before measurements.

Range of juice parameters (average of 3 vintages, 1983—85)  
Größenordnung von Saftparametern (Durchschnitt aus 3 Ernten, 1983—85)

Grape variety	Sugar (° Brix)	Total acidity (g/l)	pH
Müller-Thurgau	16–20	10– 6	3.1–3.5
Riesling	17–22	15–10	3.0–3.2

#### Headspace analysis

Analyses were carried out with a Pye Unicam PU 4500 gas chromatograph with a flame photometric detector. The volatiles were separated using an acetone washed 80—100 mesh Poropak QS column with temperature programming (5 min at 80 °C, 12 °C/min). Mass calibration was achieved with permeation tubes (O'KEEFE and ORTMAN 1966).

#### Chemicals and peak identification

Standard sulphur chemicals were CS<sub>2</sub> (Riedel-de Haën, Germany), OCS (Matheson, USA) and DMS (Hopkins and Williams, England). SO<sub>2</sub> was obtained from sodium metabisulphite (BDH, England). Peaks were identified using a collection trap, effluent splitter and mass spectrometry (YOUNG 1981; KNOWLES 1985).

### Results and discussion

Figs. 1 and 2 display the changes of sulphur volatiles CS<sub>2</sub> and OCS within 72 h after extracting juices from Müller-Thurgau grapes. They are also representative of the levels monitored in Riesling juices. It should be noted that comparable sulphur gas evolution curves were obtained for other vintages regardless of the grape type or maturity. Greater evolution of both OCS and CS<sub>2</sub> was observed at the higher temperature, presumably a manifestation of metabolic rates. Considering firstly the samples maintained at 30 °C, the figures reveal an immediate and constant increase of the levels of both sulphur components from the moment of crushing onwards. After about 36 h, wild yeasts in the sample began to ferment, which very quickly reduced the levels of the

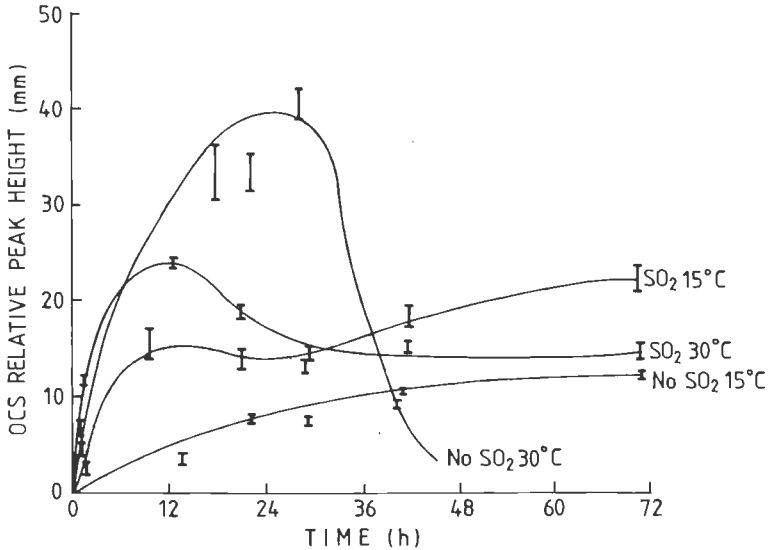


Fig. 1: The formation of OCS, as observed by headspace analysis, during clarification of Müller-Thurgau juice with and without SO<sub>2</sub> at 15 and 30 °C.

Die Bildung von OCS während der Entschleimung von Müller-Thurgau-Most mit und ohne SO<sub>2</sub> bei 15 und 30 °C. Nachweis durch Dampfzellanalyse.

sulphur volatiles. Samples kept at 15 °C behaved differently as volatile sulphur concentrations increased more slowly. Even after 72 h, fermentation had not started and a reduction of the concentrations was not observed.

The presence of SO<sub>2</sub> had no apparent effect on the generation of OCS and CS<sub>2</sub> prior to the onset of fermentation. Fig. 1 is anomalous in this regard, in that OCS production was apparently greater for the case where SO<sub>2</sub> was added and the temperature maintained at 15 °C. However, inspection of OCS evolution curves for other vintages and also other grape maturity for this vintage confirm that SO<sub>2</sub> has in fact no influence.

These results foremost confirm the incidence of OCS in grape juices (SPEDDING *et al.* 1980). Additional information has been established concerning its occurrence during the clarification of grape juices over a period of up to 72 h. Its extremely low boiling point of -50 °C could account for its rapid removal, purged by the CO<sub>2</sub> gas of the fermentation for example, although it is equally possible that the yeast might have consumed some during its growth prior to fermentation. Many wineries clarify juices by centrifugation immediately after extraction or by cold-settling at temperatures close to 0 °C. Whether under such conditions OCS could be formed needs further investigation. Concentrations of OCS are given only as relative peak height as its quantification by means of a permeation tube was unsuccessful. An OCS gas sample could not be obtained without impurities.

Fig. 2 for the first time presents information on the occurrence of carbon disulphide (CS<sub>2</sub>) during the clarification of grape juice. As it was clearly identified by mass spectrometry (KNOWLES 1985), we can only speculate as to its origin. Pure CS<sub>2</sub> is a liquid of 50 °C boiling point with a sweet, ethereal odour. Usually commercial grades smell foul due to the presence of unknown impurities. Similar to OCS, CS<sub>2</sub> is emitted from

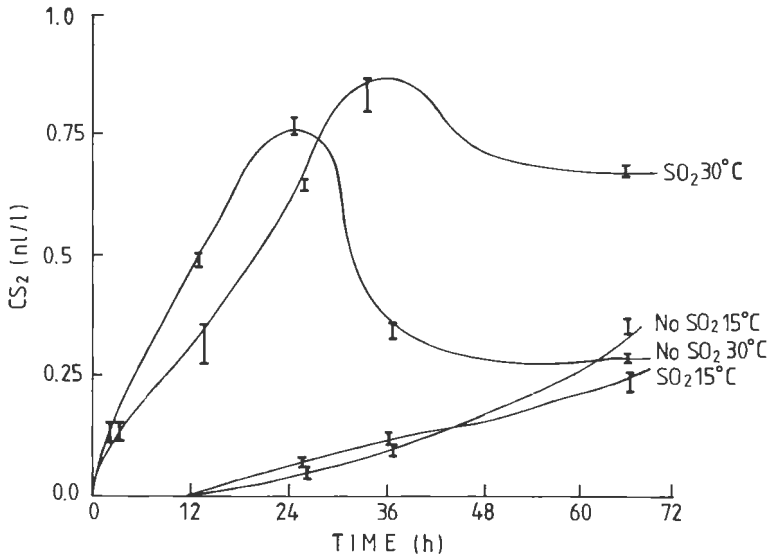


Fig. 2: The formation of CS<sub>2</sub> during clarification of Müller-Thurgau juice with and without SO<sub>2</sub> at 15 and 30 °C, where CS<sub>2</sub> concentrations refer to headspace analyses.

Die Bildung von CS<sub>2</sub> während der Entschleimung von Müller-Thurgau-Most mit und ohne SO<sub>2</sub> bei 15 und 30 °C. Nachweis durch Dampfzuchtanalyse.

decaying vegetation (ANEJA *et al.* 1979). This seems to be the most plausible explanation for its occurrence. The unclarified grape juice contains severely damaged vegetable matter in the first stages of decay.

All of the results shown in Figs. 1 and 2 refer to concentrations of sulphur volatiles in the headspace gas above the liquid phase. Measurement of partition coefficients for CS<sub>2</sub> shows that variations in headspace gas concentrations are not solely caused by temperature changes from 15 to 30 °C. This in itself would only allow for a 1.7 times increase. Further, as OCS is so extremely volatile aqueous standards were not feasible. There are no data available in the literature on such coefficients, either in wine or grape juice. The strong increase at 30 °C in concentrations of both OCS and CS<sub>2</sub> with or without SO<sub>2</sub> addition until fermentation commenced as well as the slow but steady increase at 15 °C could be explained as biochemical reactions activated by the crushing of the grapes. The much accelerated formation at 30 °C would thus be favoured. However, chemical precursors of these volatile compounds are still unknown.

In a previous publication we have already reported the incidence of dimethyl sulphide (DMS) in several grape juices (SPEDDING *et al.* 1980). During the present investigations DMS was found only on four occasions and only when juices had begun to ferment. More juices will have to be monitored to establish whether DMS is formed by purely chemical reactions or is the result of the activity of microorganisms. The evolution of the volatile sulphur components would exert an unknown influence on the organoleptic characteristics of the juice. However, certainly the OCS and DMS contributions will be negligible. Finally, the removal at this stage of the more easily volatilized sulphur constituents would have an unknown effect on subsequent dimethyl sulphide formation during wine production. These are matters requiring further investigation.

### Summary

The evolution of the sulphur gases OCS, CS<sub>2</sub> and DMS was monitored during the clarification of freshly harvested juices from Müller-Turgau and Riesling. Immediately after crushing OCS and CS<sub>2</sub> levels began to increase, substantially favoured by high temperatures. When fermentation started concentrations decreased. DMS was found only in fermenting juices.

### References

1. ANEJA, V. P.; OVERTON, J. H.; CUPITT, L. T.; DURHAM, J. L.; WILSON, W. E.; 1979: Carbon disulphide and carbonyl sulphide from biogenic sources and their contributions to the global sulphur cycle. *Nature* **282**, 493—496.
2. BAMFORTH, C. W.; 1985: Biochemical approaches to beer quality. *J. Inst. Brew.* **91**, 154—160.
3. CHUNG, T. Y.; HAYASE, F.; KATO, H., 1983: Volatile components of ripe tomatoes and their juices, purées and pastes. *Agricult. Biol. Chem.* **47**, 343—351.
4. DICKENSON, C. J.; 1983: Dimethylsulphide — its origin and control in brewing. *J. Inst. Brew.* **89**, 41—46.
5. KNOWLES, S. J.; 1985: Dimethyl Sulphide in Wine. Master of Science Thesis, University of Auckland, New Zealand.
6. DE MORA, S. J.; ESCHENBRUCH, R.; KNOWLES, S. J.; (the late) SPEDDING, D. J.: The formation of dimethyl sulphide during fermentation using a wine yeast. *Food Microbiol.* (in press).
7. O'KEEFE, A. E.; ORTMAN, G. C.; 1966: Primary standards for trace gas analysis. *Anal. Chem.* **38**, 760—763.
8. SHAW, P. E.; NAGY, S.; 1981: Analysis and flavour effects of volatile sulphur compounds in citrus juices. In: CHARALAMBOUS, G.; INGLETT, G. (Eds.): *The Quality of Foods and Beverages. Chemistry and Technology. Vol. 1*, 361—376. Academic Press.
9. SPEDDING, D. J.; ESCHENBRUCH, R.; PURDIE, A.; 1980: The distribution of dimethyl sulphide in some New Zealand wines. *Vitis* **19**, 241—245.
10. WILLIAMS, R. S.; GRACEY, D. E. F.; 1982 a: Factors influencing the levels of polysulfides in beer. *Amer. Soc. Brew. Chem. J.* **40**, 71—74.
11. — — —; 1982 b: Beyond dimethyl sulfide: The significance to flavour of thioesters and polysulfides in Canadian beers. *Amer. Soc. Brew. Chem. J.* **40**, 68—71.
12. WURDIG, G.; 1985: Aromaböckser im Wein. *Dt. Weinbau* **40**, 341. (Abstr.).
13. YOUNG, H.; 1981: Direct desorption of traps for capillary column gas chromatography. *J. Chromatography* **214**, 197—201.

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