Dimethyl sulfide – Significance, Origins and Control[1]

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ABSTRACT

Dimethyl sulfide (DMS) is a substantial contributor to the aroma of many lager-style beers. Opinion varies on its desirability. It can be derived in beer from two sources: the thermal decomposition of S-methylmethionine (SMM) produced in the embryo of barley during germination; (b) the reduction of dimethyl sulfoxide (DMSO, derived from the breakdown of SMM during the curing of malt) by yeast. The enzyme that effects DMSO reduction is a reductase whose primary function is the reduction of methionine sulfoxide and which competes for reducing power with several other cellular systems. Control of DMS production from SMM is achieved by specifying precursor levels in malt, by attending to the vigor and duration of the boil and by controlling the length of the whirlpool stand. Control of DMS production from yeast is achieved by specifying yeast strain, wort gravity, free amino nitrogen and pH, the type of fermenter (ergo the extent of volatilization) and the fermentation temperature.

Key words: Control, Dimethyl sulfide, dimethyl sulfoxide, malt, S-methyl methionine, yeast

Dimethyl sulfide (DMS, Fig 1a) is a ubiquitous molecule in nature. It plays a significant role in the cycling of sulfur in nature (as articulated in the Gaia Hypothesis, 31). Stages in the S cycle include the hydrolysis of dimethylsulfoniopropionate by algae to DMS, the oxidation of the latter atmospherically inter alia to dimethyl sulfoxide (DMSO), and reduction of the latter microbially (43). It has been claimed that DMS is used by seabirds to navigate towards food-rich areas (35)

Not only does the highly volatile DMS (boiling point 38°C) comprise a characteristic odor in marine districts, it also plays a key role in the aromas of a range of foodstuffs, including asparagus (47), beetroot (38), corn (13), cabbage (33), tea (26), cocoa (29), milk (41), wine (30), rum (28) and seafoods (37).

DMS was first considered as a relevant molecule in beer by Sinclair et al (44) who showed that there were substantially higher levels of DMS in lagers than in ales. The correlation between perceived lager character and levels of DMS was first drawn by Anderson et al (1).

The flavor threshold for DMS will differ between beers, depending on their complexity, but it is generally quoted as being around 30µg/L. Brewers differ substantially in their liking or otherwise for DMS, ranging from those who strive to ensure levels substantially below the flavor threshold, through to one North American lager brand that contains substantially more than 100 µg/L. Excessive DMS may introduce a canned corn or blackcurrant bud note to beer. There may not necessarily be a simple direct correlation between the levels of DMS in beer and perceived DMS character: for instance, phenyl ethanol and phenyl ethyl acetate tend to mask the perception of DMS (23).

Origin of DMS in beer

White and colleagues showed that there is a low molecular weight, cationic and heat labile molecule in malt which generates DMS upon heating (48, 49). They showed the precursor could be measured by heating samples in caustic and measuring the resultant DMS. White went on to claim that the precursor comprised S-methylmethionine attached to an unidentified material that stained with ninhydrin (50). He suggested that the precursor as isolated from green malt could not be metabolized by yeast but kilning at temperatures in excess of 75°C led to the development of a form of this entity that could be converted to DMS by yeast.

It was Dickenson (14, 15) who established that the heat-labile DMS precursor that develops during the germination of grain is S-methylmethionine (SMM) per se (Fig 1b).

Anness and Bamforth (5) established that the material produced in kilning that could be converted to DMS by yeast is DMSO (Fig 1c). Anness (2, 3) showed that DMSO is extensively present in malts and worts, the more so the higher the kilning temperature. Bamforth (7) demonstrated that the enzyme involved is methionine sulfoxide reductase, a three component system involving a sulfoxide reductase that is fed with reducing power by the protein couple thioredoxin and thioredoxin reductase. Sulfoxide reductase is only one recipient of electrons from the thioredoxin system (6; Fig 2). Other draw offs include for ribonucleotide reductase (18), protein disulfide reductase (32) and sulfate reductase (40).

The precise mechanism that a cell employs to regulate the flow of hydrogen to the various demands is unclear, but it is to be expected, for instance, that a requirement for an increased supply of deoxyribonucleotides for DNA synthesis during cell division is likely to decrease the availability of reducing power for sulfoxide reduction.

Dickenson (16) expressed doubt that DMSO was particularly significant as a precursor of DMS in beer. However Leeemans et al (27) used deuterated DMSO to show that 80% of the DMS in the lager beer under investigation originated in DMSO. Furthermore Hansen (22) demonstrated that yeast mutants lacking sulfoxide reductase gave much lower amounts of DMS after fermentation. Samp et al drew attention to a likely role for mitochondria in the ability of yeast to reduce DMSO (42).

Anness and Bamforth also confirmed that DMSO can be reduced to DMS quantitatively by wort-spoilage bacteria (4). Zinder and Brock (52) were the first to highlight the ability of a diversity of bacteria and other microorganisms to reduce DMSO to DMS. As such, DMS production may result from the spoilage of beer as well as wort and is likely to be significant in a range of beers that involve a diversity of organisms, e.g. lambic-style products.

The production of DMS from S-methylmethionine

SMM is not present in raw barley but is synthesized in the embryo during germination (49). The enzyme that effects this synthesis is S-Adenosyl-L-Methionine: L-Methionine S-Methyltransferase (39).

The extent of SMM development in the embryo depends on several factors. Barley variety has a role to play (25, 36, 49) although this may simply be on account of differences in the following parameters (4): (a) modifiability; (b) nitrogen content – with more N meaning more SMM; (c) vigor of the grain. Any factor that promotes germination (e.g. use of gibberellic acid, increased temperature in steeping and germination) will tend to promote SMM synthesis. Parameters inhibiting embryo development, e.g. the use of potassium bromate, will lessen SMM levels in green malt (48).

SMM, being heat-labile, breaks down during kilning, releasing DMS, the majority of which is driven off with the exhaust gases (4). At the initial lower temperatures on the kiln, e.g. 65°C, some 40% of the DMS produced remains in the malt. At the higher curing temperatures the rate of conversion of SMM to DMS increases (17). Kiln design significantly impacts SMM levels through the impact on SMM degradation and DMS volatilization. Increased bed depth lessens the survival of SMM on the kiln whereas increasing the flux of air through the bed increases SMM levels in the finished malt (24). During curing there is also an increased formation of DMSO (5).

The DMS surviving kilning and which is present in malt is lost during brew house operations and accordingly there is no value to specifying free DMS in malt. SMM is dissolved from malt during mashing, but the precise extent of its conversion to DMS is very much dependent on the temperature regimes involved as well as pH. The kinetics of heat-induced decay of SMM into DMS was addressed by Wilson and Booer (51) and by Dickenson (14). The latter concluded that the half of life of SMM at 100°C is 38 minutes at pH 5.2, but 32.5 minutes at pH 5.5. Table 1 illustrates the additional observation that for

every 6°C decrease in temperature, the half-life doubles. Thus while infusion mashing and lautering operations would have little impact in increasing DMS levels, decoction mashing may have the effect of increasing DMS levels in wort, depending on the precise time and temperature regime and the extent to which wort acidification is practiced. It is also pertinent to consider in this context the use of cereals such as corn that require cooking. Unsurprisingly, considering the customary reference to DMS as affording a 'cooked corn' aroma to beer, corn (maize) contains SMM that is converted to DMS upon intense heating (11). Thus the extent to which the corn is de-germed, thereby diminishing the precursor level, is highly significant.

However much more significant for DMS production from SMM are the boiling and whirlpool operations. Using his kinetic model , Dickenson developed equations to predict the free DMS level in pitching wort from the SMM level in malt (14), making the assumption that any free DMS in the sweet wort as well as that produced by decomposition of SMM in boiling is lost by evaporation. However this assumes that there is a vigorous "rolling" boil with satisfactory volatilization. In reality, if a boil represents little more than a simmer, then the purging of DMS is inefficient and this leads to substantially higher DMS levels in the pitching wort and thence the beer.

Similarly, in the hot wort receiver (whirlpool), a well-insulated system will lead to the continued breakdown of that SMM surviving the boil, but the non-turbulent conditions lead to the accumulation of DMS in the wort (25, 46, 51).

Thus the precise conditions of the kettle boil and hot wort stand have a profound effect on the extent to which SMM is degraded to DMS and in turn the extent to which DMS is driven off. Kettle configuration, vigor of the boil, extent of insulation of the whirlpool and times of transfer and residence are highly significant.

It will also be recognized that the location of a brewery can have a huge role to play. As wort boils at a lower temperature at increased elevation (reduced atmospheric pressure), there will be much less conversion of SMM to DMS in the kettle. The SMM-DMS issue must also be borne in mind when consideration is made of changing brew house systems in pursuit of energy savings (8). One strategy under increasing consideration is the stripping of volatiles, including DMS, by a gas stream, although such “wort stripping” has long been employed by some (34).

SMM is not metabolized by yeast and under most brew house regimes there will be little SMM surviving into finished beer. Pasteurization conditions are insufficiently intense to cause degradation of any SMM that does survive into the finished product.

The production of DMS from dimethyl sulfoxide

DMSO is extremely soluble in water and that which is present in the grist will be extensively extracted during mashing. DMSO is heat tolerant and has a very high boiling point (189°C) and hence is not lost in the hot brew house stages. Worts typically contain 200-400µg DMSO/L (3). Ale worts contain

at least as much DMSO as lager worts, for the DMSO is largely produced during curing on the kiln and typically ale malt will receive a more intense curing regime than will lager malt.

Whereas in simple glucose-salts medium to which DMSO is added there is an approximately 13% conversion of the precursor into DMS (4), only 4-5% of the DMSO in a wort is transformed into DMS, suggesting that there are materials present in the latter which lessen the extent to which the organism can deal with DMSO. The first relevant factor is the quantity of assimilable nitrogen in the medium. It has been demonstrated that DMS production in fermentation is increased when N availability to the yeast is lessened (4, 21). The second influence is an inhibitor present in wort, identified as methionine sulfoxide (19). This molecule is more accurately described as a competing substrate, for methionine sulfoxide has a much higher affinity for the enzyme system than has DMSO (7), which is to be expected as the enzyme most likely exists in aerobic organisms to protect against the undesirable oxidation of methionine (45).

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Both ale and lager strains of yeast are capable of reducing DMSO, although if anything it is the ale strains that possess the greater ability (2). The extent of DMS formation during fermentation is heavily dependent on temperature, with five times more DMS being produced at 8°C as compared to 25°C (2). Furthermore, yeast produces disproportionately more DMS when fermenting high gravity worts (2, 4). Significantly more DMS is produced from worts containing maltose as an adjunct sugar as opposed to glucose (42).

The fermentation of worts of increased pH leads to somewhat higher DMS levels (4). Probably of more relevance, however, is the shape and volume of the fermenter. Fermentation in open vessels leads

to much less DMS in beer as compared to beer fermented in closed vessels (1, 12). Early in fermentation there is usually a major decrease in DMS levels through stripping of DMS in the gases, making DMS one of the most significant 'contaminants' in recovered carbon dioxide. Yet rather than complete elimination of DMS, there is always a significant residuum, which we can ascribe to the production of DMS from DMSO. Indeed somewhat of an increase in DMS concentration is generally observed late in primary fermentation, presumably reflecting the reduced levels of free amino nitrogen and the attendant increased ability of yeast to reduce DMSO (see earlier). DMS production during fermentation is masked if high levels of the substance are already present in pitching wort (4). The amount of DMS present in beer represents that present in pitching wort and which survives fermentation but also that formed by yeast metabolism. It is only through the use of labeling studies that the true extent to which DMSO reduction contributes to the level of DMS in beer can be truly recognized (20, 27).

Controlling levels of DMS in beer

A summary of approaches to lessening DMS levels in beer is given in Table 2. Those seeking to increase DMS levels would clearly take the opposing strategies.

Conclusions

There are two sources of DMS in beer: SMM and DMSO. Control of DMS arising from the former is established by specifying the level of SMM in the grist, as well as temperature and residence time in the

brew kettle and the hot wort receiver. The brewer should also be mindful of the extent to which DMS is removed from wort during fermentation. Control of the amount of DMS derived from DMSO depends on regulation of yeast strain, wort composition (especially gravity, carbohydrate profile, free amino nitrogen levels and pH), the type of fermenter used and fermentation temperature.

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Table 1. The half-life of SMM at different temperatures

Temperature (°C)	**SMM half-life at pH 5.2 (min)**	**SMM half-life at pH 5.5 (min)**
100	38	32.5
94	76	65
88	152	130
82	304	260
76	608	520
70	1216	1040

Table 2. The control of DMS levels in beer

Approaches to *decreasing* DMS levels	**Be mindful of…**
Decrease the SMM level in the grist	Obvious impacts of changing the grist. Less

(replacement of malt with adjuncts, decreased modification of malt, use of rootlet inhibitor, increased intensity of kilning, select a 2-row as opposed to 6-row variety)	modification and more kilning means, for example, increased β-glucan risks
Increased duration and vigor of the kettle boil	Some concern about increased cooked character
Reduced residence time in hot wort receiver (whirlpool), including faster cast out from kettle	Impact on wort clarity. If trub is not efficiently removed then the increased turbidity can impact yeast metabolism and production of other flavor volatiles
Use of wort stripper	Will also purge other volatiles
Use of open shallow fermenters	Greater hygiene concerns
Increase in fermentation temperature	Will impact other aroma substances
Ensure an absence of DMS-producing wort spoilage microorganisms in the brew house	Will also lessen risk from non-volatile nitrosamines

Derived from reference 9

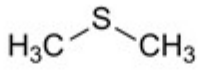
Legends to Figures

Fig 1. The molecules in this story (a) dimethyl sulfide, DMS (b) S-methylmethionine, SMM; (c) dimethyl sulfoxide, DMSO

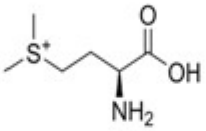
Fig 2. Competing demands for reducing power from thioredoxin. Enzymes are (A) Thioredoxin reductase; (B) Ribonucleotide reductase; (C) Protein disulfide reductase; (D) Sulfate reductase; (E) Sulfoxide reductase

Fig 1

(a)



(b)



(c)

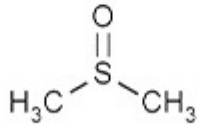
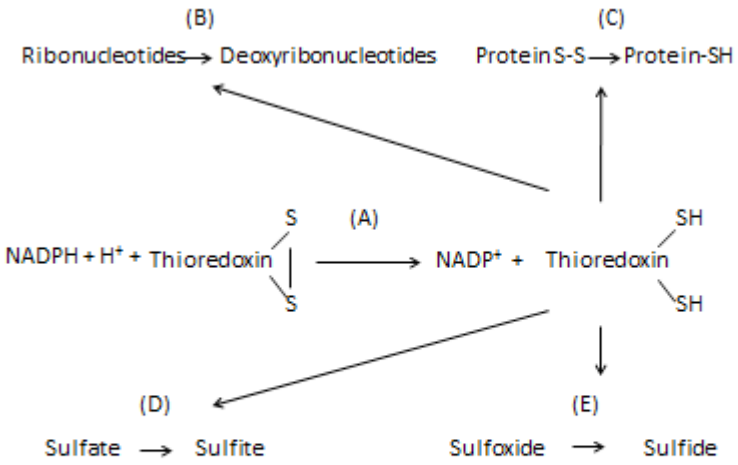


Fig 2


(B)
Ribonucleotides
Deoxyribonucleotides
(C)
Protein S-S
Protein-SH
S
(A)
SH
NADPH + H+ + Thioredoxin
NADP+ + Thioredoxin
S
SH
(D)
(E)
Sulfate
Sulfite
Sulfoxide
Sulfide