

Dimethyl Sulfide and Its Precursor in Sweet Corn

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Raw corn contained essentially no dimethyl sulfide (Me_2S). The average Me_2S content in canned or heated sweet corn samples was 8.7 p.p.m. Since the flavor threshold of this compound is in the neighborhood of a few parts per billion, Me_2S is undoubtedly one of the more important flavor constituents of heated corn. Heating in excess of the

normal canning treatment or in excess of 5 minutes of autoclaving did not result in further production of appreciable quantities of Me_2S . *S*-Methylmethionine sulfonium salt, a heat-labile compound which decomposes to yield homoserine and Me_2S , was isolated from unheated sweet corn.

The importance of dimethyl sulfide (Me_2S) to the flavor of several foods has become apparent. Since the flavor threshold is low, Me_2S can contribute to flavor at concentrations of a few parts per billion. For example, Patton *et al.* (1956) reported that its flavor threshold was 12 p.p.b. in distilled water, and Reddy *et al.* (1967) found that the flavor threshold was 19 p.p.b. in milk. Kiribuchi and Yamanishi (1963) identified Me_2S as a flavor component of green tea; heating green tea with water at 95° to 100° C. for 1.5 hours yielded about 0.25 p.p.m. of Me_2S based on the weight of the tea powder. The same authors identified the heat-labile precursor of Me_2S in green tea as *S*-methylmethionine sulfonium salt (MMS). According to Miers (1966), several parts per million of Me_2S is produced in tomatoes when they are cooked or heated, and Wong and Carson (1966) isolated MMS from tomatoes.

In addition, MMS has been isolated from asparagus by Challenger and Haywood (1954), from cabbage by McRorie *et al.* (1954), and from bracken by Bywood *et al.* (1951). Skodak *et al.* (1965) devised a method for determining MMS in plant material and obtained data for celery, tomatoes, cabbage, asparagus, and tea. Apparently, MMS is widespread in plant materials. In a recent report, Keenan and Lindsay (1968) reported the presence of MMS in raw milk and demonstrated the evolution of Me_2S when milk is heated. They suggested that the MMS in milk results from the dietary intake of plant materials by the cow.

Self *et al.* (1963) observed that Me_2S was present in the low-boiling volatiles of several cooked vegetables, including sweet corn. In another publication, the same authors

explored the mechanisms through which Me_2S can arise (Casey *et al.* 1963). Methionine when heated with pectin yielded Me_2S , and pectin was believed to function as the methyl donor in this reaction. They suggested that the reaction of methionine and pectin probably is responsible for some of the Me_2S produced in heated foods, but they were aware that MMS is also a logical precursor.

The characteristic odor of Me_2S has often been associated with canned sweet corn. The purpose of this investigation was to determine the quantity of Me_2S present in heated corn and to identify the immediate precursor.

METHODS

Determination of Me_2S . Prior to analysis for Me_2S content, sweet corn samples were thoroughly blended into a homogeneous slurry with a Virtis homogenizer. For samples of canned corn, the entire contents of the can was blended. For fresh or frozen corn, an amount of water equivalent to the amount used when canning (33 ml. of water to 66 grams of corn) was added before blending.

An autoclave was used for heat treatment of fresh or frozen corn when required. Blended samples were autoclaved in 15-cm. culture tubes sealed with Teflon-lined caps. Retention of volatile compounds in such tubes during autoclaving has been demonstrated by Bills and Keenan (1967). Tubes were cooled immediately in an ice bath following autoclaving.

Quantitative determination of Me_2S in corn samples was carried out by the on-column trapping, gas chromatographic technique developed by Morgan and Day (1965). Briefly, the analysis consisted of adding 4 grams of the blended sample to a screw-capped vial containing 5 grams of anhydrous sodium sulfate. Four milliliters of an aqueous solution of 1 p.p.m. of methyl acetate and approximately 1 mg. of solid 1-tetradecanol were added to the vial. The screw cap (modified as described by Morgan and Day) was tightened, and the contents were mixed by shaking. Methyl acetate was used as an internal standard to permit compensation for minor variations in instrument

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sensitivity between analyses, and 1-tetradecanol served as an antifoam agent. A standard curve of peak height *vs.* concentration was prepared from known concentrations of Me₂S added to a raw corn slurry (raw corn was found to be essentially free of Me₂S). Standard curves for other compounds reported in this study were prepared from known concentrations in distilled water. Since the latter compounds were present in both raw and heated corn, it was impossible to utilize the actual sample system for standard curve preparation. A collection period of 5 minutes with the sample immersed in a water bath at 50° C. and a nitrogen flow rate of 8 ml. per minute was used for preparation of standard curves and for actual analyses. A 1/8-inch o.d. by 12-foot stainless steel column packed with 20% 1,2,3-tris-(2-cyanoethoxy)propane on 80- to 100-mesh Celite 545 was employed. The column temperature was maintained at 60° C. with a carrier gas flow rate of 25 ml. per minute.

The identity of Me₂S in the samples was adequately confirmed by gas chromatographic retention time and by the mercuric chloride treatment suggested by Bassette and Whitnah (1960).

Isolation of Me₂S Precursor. One kilogram of raw corn (Jubilee variety) was blended with 1 liter of water to obtain a homogeneous slurry. The slurry was clarified by centrifugation followed by filtration of the supernatant liquid. The filtrate was percolated over carboxylic acid resin (Amberlite IRC-50) in the ammonium form at a rate of 1 liter per hour. The column was then washed thoroughly with distilled water, and the material retained on the resin was eluted with 1*N* acetic acid. The eluate was concentrated at room temperature under vacuum in a rotary evaporator until a white solid was obtained. Minimal volumes of methanol were used to dissolve the methanol-soluble material; the methanol-insoluble residue was discarded. Five parts of 2-propanol were added per part of methanolic solution, and the precipitate formed after 10 hours at 5° C. was removed by filtration and discarded. The alcoholic solution was again taken to dryness at room temperature, and the solids were dissolved in a minimal amount of water. The above is a modification of the procedure of McRorie *et al.* (1954).

Portions of the aqueous solution were applied to 0.25-mm. thin-layer plates of Silica Gel G. Another portion was made just alkaline with 1*N* sodium hydroxide, autoclaved for 20 minutes, and applied alongside the unheated portions on thin-layer plates. Solutions of authentic MMS and homoserine, the degradation product obtained in addition to Me₂S from heated MMS, were also spotted on the thin-layer plates. Solvent systems used for development of thin-layer plates are listed in Table I. Compounds separated were developed by spraying with 0.1% ninhydrin in 95% ethanol.

RESULTS AND DISCUSSION

Unblanched sweet corn (Jubilee variety) freshly cut from the cob contained essentially no Me₂S. When autoclaved for periods ranging from 5 to 60 minutes, concentrations of Me₂S in the neighborhood of 10 p.p.m., based on the weight of the corn slurry, were evolved (Table II). Autoclaving for more than 5 minutes did not produce further appreciable quantities of Me₂S.

Table I. Thin-Layer Chromatographic *R_f* Values for Authentic and Isolated *S*-Methylmethionine Sulfonium Salt

Solvent System	Ratio of Solvent Components (V./V.)	<i>R_f</i> Value	
		Authentic	Isolated
Dimethyl sulfoxide	1	0.37	0.37
Dimethyl formamide	1		
30% ammonia	2		
Ethanol	3	0.24	0.24
30% ammonia	2		
1-Propanol	3	0.14	0.15
30% ammonia	2		

Table II. Concentrations of Volatile Compounds in Jubilee Variety Sweet Corn Autoclaved for Various Times

Autoclaved, Min.	Concentration of Compound, P.P.M. ^a			
	Me ₂ S	Acetaldehyde	Acetone	Ethanol
0	<0.05	2.5	0.7	322
5	10.3	9.3	1.7	503
10	10.4	9.3	1.5	500
20	10.3	10.6	1.9	495
60	11.5	17.5	2.3	535

^a Concentration based on weight of a slurry prepared from 66 grams of corn and 33 ml. of water.

Four samples of commercially canned corn and three samples of commercially frozen corn were obtained from the market and analyzed for Me₂S content. Frozen samples were blended, autoclaved for 10 minutes, and analyzed; canned samples were blended and analyzed (Table III). The Me₂S in samples 1 to 6 ranged from 4.3 to 14.2 p.p.m., but sample 7 contained only 0.3 p.p.m. of Me₂S. Interestingly, the flavor of sample 7 resembled pumpkin or squash rather than sweet corn.

Analysis of a commercially processed can of corn and a can from the same lot which was autoclaved in the can for 30 minutes in addition to the commercial process revealed no appreciable increase in Me₂S with heating beyond the canning process. Since either commercial canning or 5 minutes of autoclaving resulted in the production of nearly the total obtainable amount of Me₂S, most of the Me₂S in heated corn probably results from a heat-labile precursor that is quickly expended.

The data in Figure 1 and Table I indicate that MMS can be isolated from sweet corn. The autoclaved aqueous solution spotted on the thin-layer plates had the characteristic odor of Me₂S and yielded a component that migrated with authentic homoserine. The unheated portion of the solution contained a component that migrated with MMS and yielded a Me₂S odor when scraped from the plate and heated. The absence of Me₂S in the unheated solution and presence in the heated solution was also confirmed by gas chromatography. Although other mechanisms are not excluded, MMS is probably of primary significance in the appearance of Me₂S in heated corn. According to Keenan and Lindsay (1968), MMS is rapidly degraded to Me₂S and homoserine at temperatures above 100° C. and nearly neutral pH.

Table III. Concentrations of Volatile Compounds in Commercial Samples of Canned and Frozen Sweet Corn^a

Sample No.	Concentration of Compounds, P.P.M.			
	Me ₂ S	Acet-aldehyde	Acetone	Ethanol
1	14.2	1.2	2.3	152
2	13.7	1.3	1.7	157
3	5.7	2.9	1.8	111
4	13.9	0.9	2.4	152
5	4.3	3.5	1.4	100
6	6.8	1.7	0.8	26
7	0.3	0.7	0.3	10

^a Frozen samples autoclaved for 10 minutes prior to analysis. Samples 1 to 4 canned, 5 to 7 frozen. Concentrations based on weight of corn slurry.

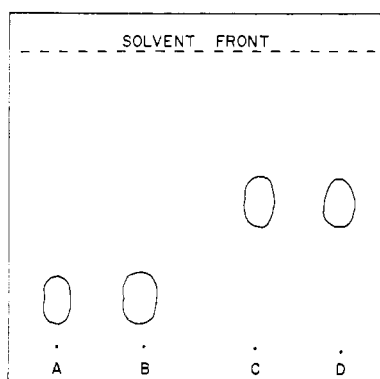


Figure 1. Thin-layer chromatographic migration

- A. Authentic S-methylmethionine sulfonium salt
 - B. Unheated component isolated from corn
 - C. Heated component isolated from corn
 - D. Authentic homoserine
- Solvent system. 3 parts of 1-propanol and 2 parts of 39% ammonia

Although of secondary interest to this investigation, three other major components were noted with regularity during the gas chromatographic analyses. The quantities of acetaldehyde, acetone, and ethanol found in the samples are presented in Tables II and III. Identification of these compounds was based only on gas chromatographic retention time; and, aside from acetaldehyde, they probably have little bearing on the flavor of corn. The odor threshold value for acetone is about 500 p.p.m. in distilled water (Wick, 1966). The authors' observations indicate that ethanol is only weakly perceived by most individuals at concentrations of 1000 to 2000 p.p.m. Acetaldehyde, however, has a flavor threshold of 1.3 p.p.m. in distilled

water according to Berg *et al.* (1955). The acetaldehyde concentration in corn increased appreciably upon heating. With heat treatments in excess of commercial processing, volatile products other than those reported herein became evident in the chromatograms. Self *et al.* (1963) noted the following volatile components and their relative abundance in cooked corn: H₂S (large), acetaldehyde (large), methyl mercaptan (small), propionaldehyde or acetone (small), ethyl mercaptan (small), and Me₂S (large). The flame-ionization detector and trapping method used in this study precluded the observation of H₂S. The mercaptans reported by Self *et al.* were not observed but could have been present as very minor components. Propionaldehyde was not found, but acetone was present in all samples, and probably was the component Self *et al.* identified as "propionaldehyde or acetone."

The high concentrations of Me₂S found in this study indicate that it is one of the important flavor constituents of sweet corn. However, the wide variation in Me₂S content among commercial samples suggests that further work is in order to investigate the parameters that influenced the yield of Me₂S in canned or cooked corn. Studies involving maturity and commercial processes such as blanching would be of interest to the packer. The plant geneticist, on the other hand, may be interested in varietal differences in Me₂S yield and the systematic breeding of corn varieties in which this compound and other flavor compounds are developed at optimum levels.

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