Natural Occurring Levels of Dimethyl Sulfoxide in Selected Fruits, Vegetables, Grains, and Beverages

Dimethyl sulfoxide (Me_2SO) was found to occur naturally in a variety of fruits, vegetables, grains, and beverages. Most of the materials tested that contained Me_2SO also contained at least a trace of its oxidized product, dimethyl sulfone.

Dimethyl sulfoxide (Me_2SO), is widely used as an industrial solvent. Chemically, Me_2SO is a highly polar, aprotic, and water-miscible organic liquid. Commercially, Me_2SO is produced by the oxidation of dimethyl sulfide (Me_2S).

At present, there are only limited reports of Me_2SO in nature. Me_2SO has been found in spearmint oil (Canova, 1971), nonfat dry milk (Ferretti and Flanagan, 1972), corn (Boyko et al., 1978), barley and malt (Anness et al., 1979), and natural waters (Andreae, 1980). Occurrence of Me_2SO in natural waters and in phytoplankton growth medium suggests it is an end product of algal metabolism (Andreae, 1980).

Me_2S is found extensively in nature and is responsible for the characteristic odor of many foods (Tressl et al., 1977; Self et al., 1963; Miers, 1966). Me_2S has been suggested as playing a major role in the natural transfer of sulfur of biological origin (Lovelock et al., 1972). Photolysis of Me_2S in air results in the formation of Me_2SO (Bentley et al., 1972). In rabbits Me_2S was found to be oxidized to dimethyl sulfone (Me_2SO_2) via Me_2SO (Williams et al., 1966a).

Me_2SO_2 has been found to occur naturally in asparagus (Tressl et al., 1977), cow's milk (Williams et al., 1966b), corn (Boyko et al., 1978), and human urine (Williams et al., 1966a). Me_2SO_2 in cow's milk is not the product of microorganisms but results from metabolism within the cow (Williams et al., 1966b). Me_2SO_2 was found in the urine of rabbits injected subcutaneously with Me_2SO (Williams et al., 1965).

The purpose of the present study was to investigate the natural levels of Me_2SO and Me_2SO_2 in a variety of fruits, grains, vegetables, and beverages. Since the natural occurrence of Me_2S is well documented in most of the materials tested, no attempt was made to measure Me_2S. Gas–liquid chromatography using a flame photometric detector was used throughout the study. Mass spectrometry was used to confirm the pressure of Me_2SO in selected materials.

EXPERIMENTAL SECTION

Materials. The fruits, vegetables, forage, and beverages examined in this investigation were either grown for the study or purchased. Those grown for the study (Table I) were plantings at Southwest Washington Research Unit (SWWRU) in Vancouver, WA, managed by Washington State University. The crops, with the exception of fruits and berries, were new plantings in 12 × 12 ft plots. All of the crops were maintained by personnel of SWWRU.

Sampling of fresh crops, either from SWWRU or the market, followed as much as possible established practices (Lykken et al., 1957). A representative sample was collected, and inedible portions such as husks, cobs, or stems were removed. The sample was then chopped and mixed, and a portion packed in a 1-qt jar or in a plastic bag and frozen until analysis. The processed samples were kept in their original containers until analyzed.

Methods. All sample preparation materials were demonstrated not to cause interferences. Extract solvents were pesticide residue grade or equivalent. Sodium chloride was reagent grade or equivalent. Celite No. 545 (Johns-Manville) and distilled water were used.

A 50-g sample was weighed into a 1-qt blender jar. A 150-mL portion of methanol and 5 g of Celite were added, and the sample was blended for 2 min. With very dry samples (grain, dry beans, tea, etc.) 50 mL of water was added prior to blending. After blending, the mixture was filtered under vacuum through Whatman No. 4 paper in an 11-cm Büchner funnel into a 500-mL flask. The filter cake was washed twice with 25-mL portions of methanol. The combined filtrate and washings were transferred to a 1000-mL round-bottom flask, and the methanol was removed on the rotary evaporator at 40 °C. The aqueous portion remaining (~40 mL) was transferred to a 250-mL separatory funnel along with 2 g of NaCl. The aqueous portion was extracted twice with 60-mL portions of hexane to remove oil and pigments. The hexane layers were discarded. The aqueous layer was transferred to a continuous extractor and extracted with 150 mL of chloroform for 22–24 h. The aqueous layer was discarded, and the chloroform evaporated on the rotary evaporator at 40 °C to ~1 mL. The residual chloroform was transferred, by using methanol washes, to a graduated centrifuge tube and brought to volume, usually 1–5 mL, so that the Me_2SO level was within the detection range.

Spiked samples were prepared by the addition of Me_2SO or Me_2SO_2 to the samples in the blender. The spiked levels were 0.1 and 1.0 ppm for Me_2SO and 0.1 ppm for Me_2SO_2. The samples were then prepared according to the aforementioned method.

Analysis. Final analysis was by gas–liquid chromatography (GLC). A Hewlett-Packard Model 5737A instrument equipped with a Meloy Laboratory flame photometric detector, with a 394-nm sulfur filter, was used. The column was 6 ft × $^1/_8$ in. o.d. Teflon packed with 15% FFAP on 40–60-mesh Chromosorb-T. The oven temperature was 160 or 180 °C isothermally for Me_2SO and Me_2SO_2, respectively. Detector temperature was 200 °C. On-column injections were used.

Preconditioning of the column was accomplished by repeated injection of 4–5 μL of sample and was found to be necessary before standards were injected. Without this preconditioning, the standards tended to produce wider peaks than the samples, especially Me_2SO.

The GLC standards of Me_2SO and Me_2SO_2 and those used for spiking samples were made by dissolving Me_2SO or Me_2SO_2 in methanol to make 1.0 mg/mL solutions. Aliquots of these solutions were diluted with methanol to make 100, 10, and 1 μg/mL solutions.

The sample concentration in parts per million (ppm) of Me_2SO or Me_2SO_2 was calculated by using the ratio of the log of nanograms (ng) of standards injected to the log of area or height of the resulting peak. This ratio was linear over a range of 6–50 ng injected, and this was considered to be the working range.

For verification of the method and the results, samples were sent to Dr. B. F. Hrutfiord at the College of Forest Resources, University of Washington, Seattle, WA. The same methodology was used as was employed in this study.

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Table I. Levels of Me_2SO and Me_2SO_2 in Materials Tested

		cultivar or type[a]	origin[a]	ppm of Me_2SO	ppm of Me_2SO_2
		Vegetables and Forage			
alfalfa	*Medicago sativa*	Serenac	A	0.10	0.07
bean	*Phaseolus vulgaris*	OSU-1604	A	tr	nd
		Red Kidney	A	nd	nd
		Blue Lake	B	nd	nd
		Red Kidney	C	nd	nd
beets	*Beta vulgaris*	a, canned	C	0.12	tr
cabbage	*Brassica oleracea* var. *capitata*	Copenhagen Market	A	0.10	tr
		a	B	0.24	nd
		a, sauerkraut	C	0.40	nd
corn	*Zea mays*	Jubilee Sweet	A	0.24	nd
		Idahybrid Field	A	0.14	nd
		Idahybrid Silage	A	0.31	nd
		a	B	0.36	tr
		a, canned 1	C	0.12	tr
		a, canned 2	C	0.14	0.11
		a, frozen	C	0.13	tr
cucumber	*Cucumis sativus*	Pioneer 1	A	0.12	nd
		Pioneer 2	A	0.07	nd
		a	B	0.26	tr
		a, pickles	C	nd	nd
oats	*Avena sativa*	a, plot 1	A	0.07	tr
		a, plot 2	A	0.14	tr
onions	*Allium cepa*	a, white	A	0.25	nd
		a, white	B	tr	nd
swiss chard	*Beta vulgaris* var. *cicla*	Rhubarb Red 1	A	0.12	0.05
		Rhubarb Red 2	A	0.15	0.18
tomatoes	*Lycopersicon esculentum*	Early Girl 1	A	0.08	tr
		Early Girl 2	A	0.11	tr
		a	B	0.16	0.20
		a, paste 1	C	2.9	0.64
		a, paste 2	C	3.7	0.86
		a, stewed	C	0.69	0.32
		Fruits			
apple	*Malus silvestris*	Puritan	A	tr	tr
		Starkrimson	A	nd	nd
		Starkrimson	B	nd	nd
orange	*Citrus sinensis*	Newton	B	nd	nd
peach	*Prunus persica*	Golden Jubilee	A	nd	nd
raspberry	*Rubus idaeus*	Haida	A	0.60	tr
		Heritage	A	0.58	tr
		Willamette	D	1.8	tr
		a, jam	C	1.8	tr
		Beverages			
beer		lager	C	1.4	0.14
coffee	*Coffea arabica*	ground roast	C	2.6	1.6
milk		whole pasteurized	C	0.13	3.3
tea	*Camellia sinensis*	black leaves	C	16.0	0.30

[a] a = variety not determined; A = fresh, from SWWRU; B = fresh, from market; C = processed, from market; D = fresh, from home garden; tr = trace; nd = not detected.

The analysis was performed with a Perkin-Elmer 3920 GLC equipped with a flame photometric detector. Mass spectrometry confirmation of Me_2SO was done on a Hitachi RMS-4 interfaced with a Perkin-Elmer 990 GLC via a jet separator.

RESULTS AND DISCUSSION

The materials tested demonstrate that Me_2SO and to a lesser extent Me_2SO_2 are widely distributed in nature (see Table I). Most of the materials tested have been reported to contain Me_2S (Tressl et al., 1977; Self et al., 1963; Miers, 1966; Dickenson, 1979; Toan et al., 1965; Kiribachi and Yamanishi, 1963). Therefore, it is not surprising that they would also contain Me_2SO and Me_2SO_2. In most cases, materials that contained Me_2SO had at least a trace of Me_2SO_2 also. Milk was the only case where the levels of Me_2SO_2 greatly exceeded that of Me_2SO.

The concentration of Me_2SO in most of the vegetables and grains tested fell in the range of a trace (<0.05 ppm) to 0.36 ppm. Only the concentrated product samples, such as tomato paste, had Me_2SO levels above 1 ppm. It was not determined whether this increase in Me_2SO content in tomato paste over whole tomatoes is a result solely of concentration or due to oxidation of Me_2S during the commercial processing. The higher levels of Me_2SO in stewed tomatoes vs. whole uncooked tomatoes suggest that some of the increase in tomato paste may be due to oxidation.

Fruits, at least the pome, stone, and citrus fruits tested, did not contain more than a trace of Me_2SO or Me_2SO_2. Raspberries, on the other hand, had very high levels of Me_2SO. The values ranged from 0.58 to 1.8 ppm, depending on the variety.

The four beverages tested all contained both Me_2SO and Me_2SO_2. The levels of Me_2SO_2 found in milk, 3.3 ppm (Table I), are similar to those reported by Williams et al. (1966b) of 6.1–8.2 ppm. Williams et al. did not find Me_2SO in milk, but they reported a detection limit of 0.5 ppm. The level of Me_2SO found in milk in this study, 0.13 ppm

(Table I), was below their detection limit.

All the materials tested except the beverages were analyzed for recovery of spiked levels of Me_2SO and Me_2SO_2. In all cases including spiked blanks, the recovery was in the range of 90–100%. The reproducibility of the method was found to be in the range of 10–15%. Me_2SO and Me_2SO_2 were not detected in the solvents or distilled water blanks.

The detection limit of Me_2SO and Me_2SO_2 was 1.2 ng at a signal-to-noise ratio of 2. This was similar to the value determined by Andreae (1980) of 1 ng (S) as Me_2SO. When a 50-g sample is used, the reported detection limit resulted in being able to detect 0.05 ppm of Me_2SO and Me_2SO_2. Any detectable value below this level was reported as a trace.

For confirmation of the analysis of Me_2SO, samples were sent to Dr. B. F. Hrutfiord at the University of Washington, Seattle, WA. Their concentrations of Me_2SO in canned corn 2, tomato paste 2, and raspberry jam were determined to be 0.16, 2.0, and 2.6 ppm, respectively. This is in agreement with the values of 0.14, 3.7, and 1.8 ppm, respectively, determined in this study (Table I). The limit of detection determined by Dr. Hrutfiord was 1.2 ng of Me_2SO with a signal-to-noise ratio of 3. Mass spectrometry was used to authenticate the presence of Me_2SO.

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Studies on Desi and Kabuli Chickpea (*Cicer arietinum* L.) Cultivars. 3. Mineral and Trace Element Composition

Eight desi and 7 kabuli type chickpea cultivars grown at the ICRISAT Center (17° N) and at Hissar (29° N) were analyzed for phosphorus, potassium, calcium, magnesium, zinc, copper, iron, and manganese. Whole seed, dhal (decorticated split cotyledons), and seed coat were analyzed. Except for calcium, zinc, and manganese, the mean values of other mineral elements of desi and kabuli whole seed and dhal samples from both the locations showed no significant differences. Seed coats of kabuli cultivars contained significantly more calcium, zinc, copper, iron, and manganese when grown at both locations and significantly more potassium and phosphorus only when grown at Hissar.

In addition to being an important source of protein, legumes are also reported to be a good source of minerals. Meiners et al. (1976) reported the content of nine mineral elements in ten kinds of raw and cooked legumes including chickpea (*Cicer arietinum* L.). The levels of minerals such as calcium, iron and phosphorus have been studied in the dry seeds of chickpea cultivars (Tiwari et al., 1977) and in developing seeds of chickpea (Lal et al., 1963; Verma et al., 1964).

Recent analyses revealed that seed coat percent and fiber content were the only two constituents that clearly distinguished the desi and kabuli types of chickpea (Jambunathan and Singh, 1980), while the amino acid composition and seed protein fractions of the two types were similar (Singh et al., 1981). Analyses of the mineral and trace element composition of desi and kabuli cultivars are reported in this communication.

MATERIALS AND METHODS

Seed samples of eight desi (USA-613, 850-3/27, Pant G-114, CPS-1, T-3, Annigeri, BG-203, and P-5462) and seven kabuli (K-4, C-104, Rabat, L-550, GL-629, Giza, and No. 501) cultivars of chickpea grown at the ICRISAT Center (near Hyderabad) (17° N; soil type vertisol) and at Hissar (29° N; soil type entisol) were obtained by pooling seeds from single plots and were received from our

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