

methylpyrazine, 5910-89-4; 2-ethyl-6-methylpyrazine, 13925-03-6; 2-ethyl-5-methylpyrazine, 13360-64-0; trimethylpyrazine, 14667-55-1; 2-ethyl-3,5-dimethylpyrazine, 13925-07-0; 2-ethyl-3,6-dimethylpyrazine, 13360-65-1; 2,6-diethylpyrazine, 13067-27-1; tetramethylpyrazine, 1124-11-4; 2-ethenyl-5-methylpyrazine, 13925-08-1; 2-ethenyl-6-methylpyrazine, 13925-09-2; 2,3-diethyl-5-methylpyrazine, 18138-04-0; 2-methoxy-3-(1-methylpropyl)pyrazine, 24168-70-5; 2-methoxy-3-(2-methylpropyl)pyrazine, 24683-00-9; 2-propyl-3,6-dimethylpyrazine, 18433-97-1; 2-methoxy-3-butylpyrazine, 32737-11-4; 1,2,3-triazolo[1,5-a]pyrazine, 51392-75-7; 2-(3-methylbutyl)-3,6-dimethylpyrazine, 18433-98-2; (E)-5-methyl-2-(1-propenyl)pyrazine, 18217-82-8; D-fructose, 57-48-7.

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Comparison of the Volatile Compounds Obtained from Thermal Degradation of Cysteine and Glutathione in Water

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The thermal degradation of both cysteine and glutathione was studied in a closed model system. Aqueous solutions of each reactant were adjusted to pH 7.5 and heated at 180 °C, representing frying temperature. From the degradation of cysteine, 34 volatile compounds were identified and the major products were 2,4,6-trimethylperhydro-1,3,5-thiadiazine and 2,4,6-trimethylperhydro-1,3,5-dithiazine. Of the 17 compounds identified as products of glutathione degradation, the isomers of 3,5-dimethyl-1,2,4-trithiolane were the major products.

Hydrogen sulfide is an important reactant in the production of meat flavors (MacLeod, 1987). It is liberated

from cysteine, cystine, and glutathione (γ -Glu-Cys-Gly) when meat is heated. Glutathione releases hydrogen sulfide rapidly during the early stages of cooking (Mecchi et al., 1964; Ohloff et al., 1985).

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The question of whether Maillard reaction products derived from peptides differ from those derived from their constituent amino acids has been raised by Nursten (1987). The effect of pH on the volatile components formed from a dilute aqueous solution of cysteine heated at 160 °C for

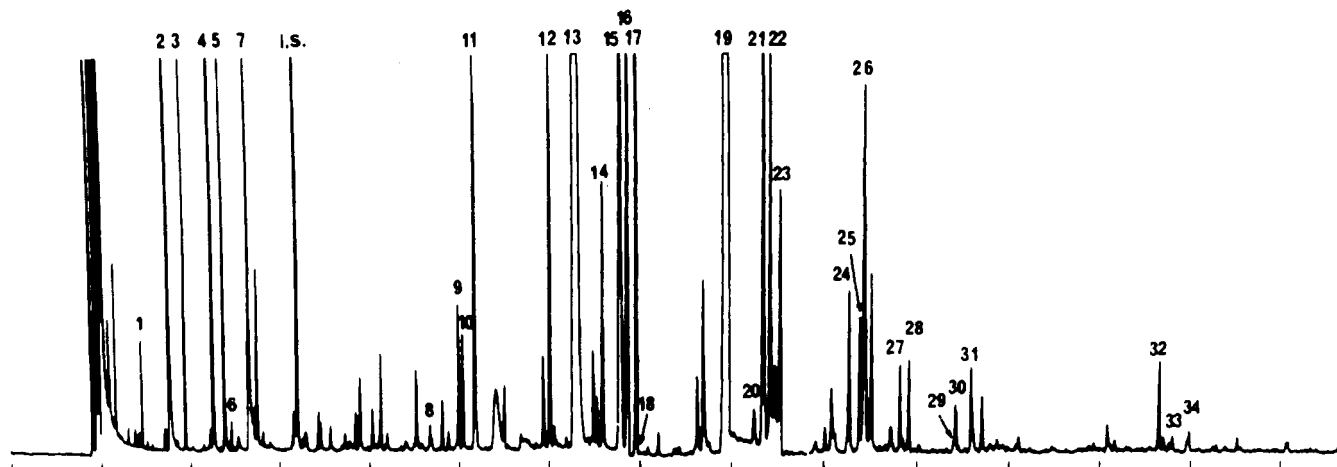


Figure 1. GC profile of the volatiles from the degradation of cysteine.

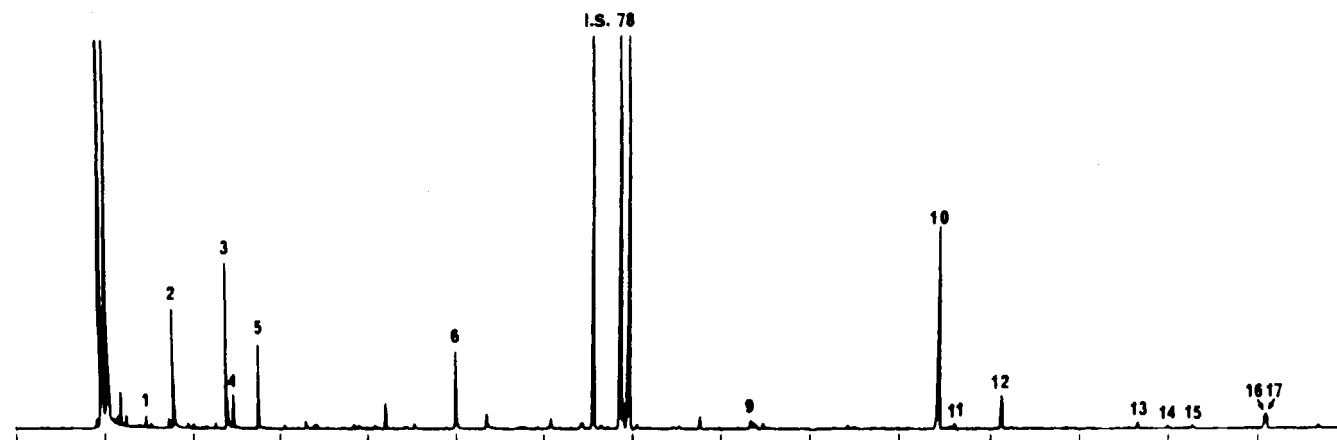


Figure 2. GC profile of the volatiles from the degradation of glutathione.

30 min has been reported by Shu et al. (1985). At pH 5.1 and 7.1, 3,5-dimethyl-1,2,4-trithiolanes, which possess roasted odors, are the major components. There are no literature data pertaining to volatile components generated from the thermal decomposition of glutathione. In the present paper, the volatile compounds generated from the thermal decomposition of glutathione in water were compared to those of cysteine in water.

EXPERIMENTAL SECTION

Sample Preparation. A 600-mg portion (0.05 mol) of cysteine (reagent grade, Sigma Chemical Co., St. Louis, MO) or 1500 mg (0.05 mol) of glutathione (reduced form, reagent grade, Sigma) was dissolved in 100 mL of distilled water. The mixtures were adjusted to pH 7.5 with 1 N NaOH, added to a 0.3-L Hoke SS-DOT sample cylinder, and sealed. The mixtures were heated at 180 °C in an oil bath for 1 h. The reaction mass was then simultaneously steam-distilled and extracted into diethyl ether by a Nickerson-Likens apparatus. An internal standard was added to each sample before steam distillation, 0.4 μ L of 4-heptanone for cysteine and 1.0 μ L of ethyl heptanoate for glutathione. The distillates were dried over anhydrous sodium sulfate and concentrated under a stream of nitrogen to a final volume of 0.2 mL.

Gas Chromatographic Analysis. A Varian 3400 gas chromatograph equipped with a fused silica capillary column (60 m \times 0.25 mm (i.d.), 0.25- μ m thickness, DB-1; J&W) and a flame ionization detector were used to analyze the volatile compounds isolated from the heated reaction system. The operation conditions were as follows: injector temperature, 230 °C; detector temperature, 260 °C; helium

carrier flow rate, 1 mL/min; temperature program, 40–220 °C at 2 °C/min and held at 220 °C for 10 min. A split ratio of 50:1 was used.

Linear retention indices for the volatile compounds were calculated with *n*-paraffin standards C₈–C₂₂; Alltech Associates) as references (Majlat et al., 1974).

GC/MS Analysis. The concentrated samples were analyzed by GC/MS by a Varian 3400 gas chromatograph coupled to a Finnigan MAT 8230 high-resolution mass spectrometer equipped with an open split interface. GC conditions were the same as described above. Mass spectra were obtained by electron ionization at 70 eV and a source temperature of 250 °C. The filament emission current was 1 mA, and spectra were recorded on a Finnigan MAT SS 300 data system.

NMR Analysis. The sample was dissolved in CDCl₃ and spectrum derived at ambient temperature on a Varian EM-360L 60-MHz NMR spectrometer.

RESULTS AND DISCUSSION

Figures 1 and 2 show the gas chromatographic profiles on a DB-1 column of the volatile compounds obtained from the degradation of dilute aqueous solution of cysteine and glutathione, respectively, at pH 7.5 and 180 °C. The components identified from these samples with their peak identification numbers, retention indices, and quantitative data are compiled in Table I. The volatiles were identified by comparing their retention indices and mass spectra with those of authentic compounds and published literature data (Boelens et al., 1974; Kleipool and Tas, 1974; Vitzthum and Werkhoff, 1974; Heller and Milne, 1978; Nixon et al., 1979; Ten Noever de Brauw et al., 1983).

Table I. Volatile Compounds Identified from Thermal Degradation of Cysteine and Glutathione

compound identified	MW	I_r (DB-1)	cysteine (A)		glutathione (B)	
			peak no.	mg/mol	peak no.	mg/mol
thiophene	84	648	1	4.8	1	2.5
thiazole	85	707	2	155.6	2	23.2
pyrrole	67	727	3	23.7		
2-methylthiazole	99	763	4	100.5	3	33.7
4-methylthiazole	99	777	5	36.1	4	4.2
2-methylpyridine	93	787	6	2.1		
5-methylthiazole	99	814	7	47.8	5	11.5
2-methyl-1,3-dithiolane	120	958	8	3.2		
2-acetylthiazole	127	980	9	13.4	6	tr ^a
2-methyl-5-ethylthiazole	127	983	10	10.9		
2,4,6-trimethylperhydro-1,3,5-oxathiazine	147	992	11	53.9		
3-methyl-2-formylthiophene	126	1046	12	43.0		
2,4,6-trimethylperhydro-1,3,5-thiadiazine	146	1056	13	1257.2		
2,4,6-trimethylperhydro-1,3,5-thiadiazine	146	1084	14	27.6		
2-(1-oxopropyl)thiazole	141	1096	15	123.9		
3,5-dimethyl-1,2,4-trithiolane	152	1101	16	94.8	7	267.2
3,5-dimethyl-1,2,4-trithiolane	152	1108	17	91.0	8	248.2
4,6-dimethylperhydro-1,2,3,5-trithiazine	167	1110	18	tr		
2,4,6-trimethylperhydro-1,3,5-dithiazine	163	1174	19	1466.7		
3-methyl-1,2,4-trithiane	152	1198	21	77.5	9	7.4
2,4,6-trimethylperhydro-1,3,5-dithiazine	163	1204	22	41.7		
2,4,6-trimethylperhydro-1,3,5-dithiazine	163	1211	23	29.1		
2,4-dimethyl-6-ethylperhydro-1,3,5-dithiazine	177	1262	24	17.6		
2,6-dimethyl-4-ethylperhydro-1,3,5-dithiazine	177	1269	25	12.4		
2,6-dimethyl-4-ethylperhydro-1,3,5-dithiazine	177	1273	26	58.1		
2,4,6-trimethyl-1,3,5-trithiane	180	1299	27	9.9		
2,4,6-trimethyl-1,3,5-trithiane	180	1306	28	8.9		
3,6-dimethyl-1,2,4,5-tetrathiane	184	1343	29	tr	10	140.4
3,6-dimethyl-1,2,4,5-tetrathiane	184	1346	30	5.8	11	2.8
4,6-dimethyl-1,2,3,5-tetrathiane	184	1356	31	11.0	12	26.5
1,2,5-trithiepane	152	1499			13	4.3
3,5,7-trimethyl-1,2,4,6-tetrathiepane	212	1511	32	9.9	14	tr
3,5,7-trimethyl-1,2,4,6-tetrathiepane	212	1526	33	tr	15	2.2
3,5,7-trimethyl-1,2,4,6-tetrathiepane	212	1538	34	1.6		
4,7-dimethyl-1,2,3,5,6-pentathiepane	216	1626			16	20.8
4,7-dimethyl-1,2,3,5,6-pentathiepane	216	1628			17	20.9

^aTrace.

Table II. Mass Spectral Data of Sulfur-Containing Compounds Identified

compound	MS data, m/z (rel intens)
2-methyl-1,3-dithiolane	120 (100), 105 (80), 59 (56), 45 (62), 60 (51), 71 (38), 92 (35), 112 (30); M_r 120
2,4,6-trimethylperhydro-1,3,5-oxathiazine	44 (100), 103 (21), 60 (20), 43 (9), 42 (8), 70 (7), 45 (7), 147 (2); M_r 147
2,4,6-trimethylperhydro-1,3,5-thiadiazine	44 (100), 70 (55), 42 (40), 43 (18), 103 (15), 41 (1), 61 (10), 146 (3); M_r 146
3,5-dimethyl-1,2,4-trithiolane	59 (100), 64 (77), 92 (75), 152 (72), 60 (61), 45 (55), 88 (42), 154 (9); M_r = 152
4,6-dimethylperhydro-1,2,3,5-trithiazine	71 (100), 70 (62), 56 (58), 135 (43), 42 (42), 44 (30), 64 (12), 167 (2); M_r 167
2,4,6-trimethylperhydro-1,3,5-dithiazine	44 (100), 163 (32), 71 (31), 70 (26), 60 (25), 59 (22), 103 (15), 140 (6), 165 (3); M_r 163
3-methyl-1,2,4-trithiane	60 (100), 59 (86), 152 (80), 87 (55), 45 (45), 92 (42), 44 (40), 64 (36), 70 (12), 119 (5); M_r 152
2,4-dimethyl-6-ethylperhydro-1,3,5-dithiazine	44 (100), 58 (83), 177 (27), 70 (26), 84 (24), 41 (23), 117 (8), 74 (7), 149 (2); M_r 177
2,6-dimethyl-4-ethylperhydro-1,3,5-dithiazine	44 (100), 71 (40), 42 (34), 70 (25), 59 (22), 177 (12), 60 (14), 103 (10); M_r 177
2,4,6-trimethyl-1,3,5-trithiane	55 (100), 43 (78), 45 (62), 60 (53), 59 (47), 180 (46), 88 (25), 115 (25), 64 (24), 92 (23), 116 (20), 182 (5); M_r 180
3,6-dimethyl-1,2,4,5-tetrathiane	59 (100), 60 (57), 43 (33), 184 (32), 124 (24), 45 (22), 41 (20), 64 (19), 119 (11), 92 (6), 186 (6); M_r 184
4,6-dimethyl-1,2,3,5-tetrathiane	59 (100), 60 (53), 184 (30), 124 (27), 45 (21), 119 (17), 64 (16), 92 (5), 186 (5), 87 (4), 152 (1); M_r 184
1,2,5-trithiepane	152 (100), 59 (87), 88 (84), 92 (69), 60 (57), 45 (40), 87 (32), 64 (25), 154 (12); M_r 152
3,5,7-trimethyl-1,2,4,6-tetrathiepane	152 (100), 88 (87), 59 (79), 92 (71), 60 (56), 43 (41), 45 (35), 87 (28), 64 (25), 212 (12); M_r 212
4,7-dimethyl-1,2,3,5,6-pentathiepane	92 (100), 156 (82), 59 (57), 64 (45), 152 (44), 43 (38), 45 (30), 216 (8); M_r 216

The structure assignment for 2,4,6-trimethylperhydro-1,3,5-thiadiazine, a newly identified component in cysteine degradation products, was based on the comparison of its NMR spectral data with those reported by Boelens and co-workers (1974). 2,4,6-Trimethylperhydro-1,3,5-thiadiazine has been obtained by reacting bis(1-mercaptoethyl) sulfide with ammonia at room temperature. The same compound was also detected in the reaction mixture of acetaldehyde, hydrogen sulfide, and ammonia (molar ratio 1:1:1) in a closed glass vessel (Boelens et al., 1974). 2,4,6-Trimethylperhydro-1,3,5-thiadiazine has been reported to decompose on preparative GC (Boelens et al.,

1974), but it was stable enough during the present fused silica capillary column GC/MS analysis to yield a good mass spectrum. 2,4,6-Trimethylperhydro-1,3,5-thiadiazine has recently been reported to decompose largely to 2,4,6-trimethylperhydro-1,3,5-dithiazine during storage and has been described as having strong roast cereal and popcornlike notes (Kawai et al., 1985).

In both cysteine and the glutathione degradation systems, all the compounds identified were heterocyclic compounds (Table I). With the exception of 2-methylpyridine and pyrrole, they all contain one or more sulfur atoms in the heterocyclic ring. Table II lists the mass

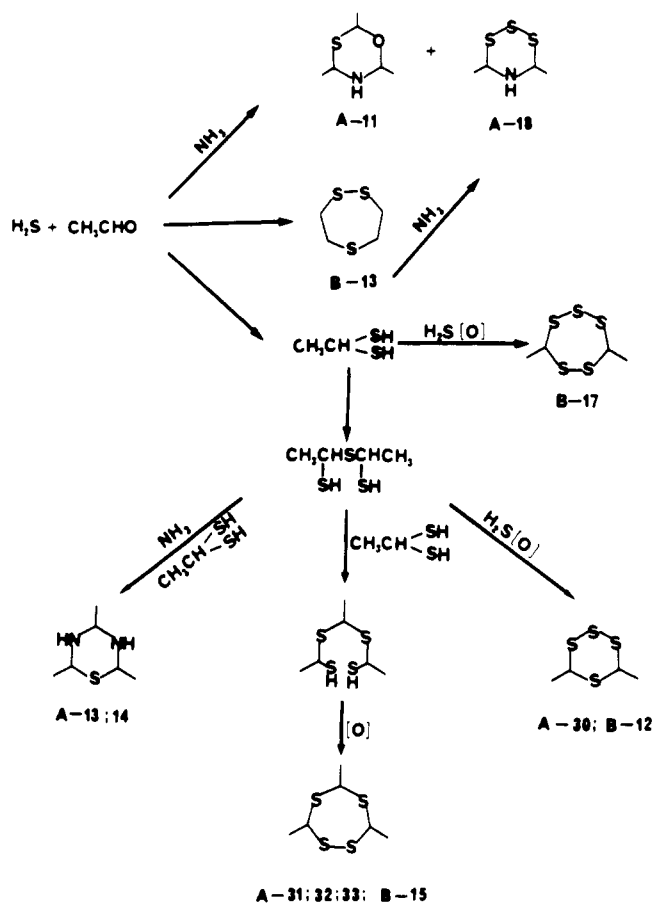


Figure 3. Possible mechanism of the formation of sulfur-containing compounds from cysteine (A) and glutathione (B) degradation. Numbers refer to the peak numbers in Figures 1 and 2.

spectral data for the cyclic sulfur-containing compounds identified.

The structures and possible formation mechanisms for the newly identified cyclic sulfur-containing compounds are illustrated in Figure 3.

The identification of these novel sulfur-containing compounds, especially the observation of 2,4,6-trimethylperhydro-1,3,5-thiadiazine, strongly supports the mechanism postulated by Boelens and co-workers (1974) for the formation of sulfur-containing compounds in food flavors. It is interesting that 2,4-dimethyl-6-ethylperhydro-1,3,5-dithiazine and 2,6-dimethyl-4-ethylperhydro-1,3,5-dithiazine were identified in the reaction mixture of cysteine degradation. According to the mechanism of Boelens and co-workers (1974), propanal is involved in the formation of these two dithiazines. This leads to the assumption that the commercial cysteine contained impurities that generated propanal upon thermal decomposition. The possibility that propanal is formed by thermal degradation of cysteine cannot be excluded.

Of the cyclic polysulfides identified in this study, four have been identified in food flavors. 3,5-Dimethyl-1,2,4-trithiolane was first identified by Chang and co-workers (1968) in the volatiles of boiled beef and has subsequently been found in the volatiles of cooked chicken (Horvat, 1976; Tang et al., 1983), mutton (Nixon et al., 1979), and potato (Buttery et al., 1970). It is reported to have roasted and onionlike flavors (Fors, 1983; Shu et al., 1985). Thialdine (2,4,6-trimethylperhydro-1,3,5-dithiazine) has been identified among the volatiles of cooked beef (Brinkman et al., 1975; Wilson and Katz, 1975), lamb fat (Buttery et al., 1977), mutton (Nixon et al., 1979), antarctic

krill (Kubota et al., 1980), and fried chicken (Tang et al., 1983) and has been reported to have a typical aroma of heated meat (Ohloff and Flament, 1978) and roast shrimp (Kawai et al., 1985). 2,4,6-Trimethyl-1,3,5-trithiane is described as having dusty, earthy, and nutty notes and has been detected in cooked chicken flavor (Pippen and Mecchi, 1969; Tang et al., 1983). 3,6-Dimethyl-1,2,4,5-tetrathiane has been identified among the volatiles of cooked mutton (Nixon et al., 1979). Although none of the other cyclic polysulfides identified have been found in food flavors, many of their parent analogues including 1,2,3,5-tetrathiane, 1,2,4,5-tetrathiane, 1,2,4,6-tetrathiepane, and 1,2,3,5,6-pentathiepane have recently been reported as volatiles of the Shiitake mushroom (Chen and Ho, 1986).

When cysteine was degraded in water at pH 7.5 for 1 h, 34 compounds were identified and the yield of the volatiles obtained was 3.84 g/mol of cysteine. Under the same conditions, only 17 compounds were identified from glutathione degradation and the yield of the volatiles obtained was 0.82 g/mol of glutathione. The lower yield and small number of compounds generated strongly suggest that the degradation of glutathione is much milder than that of cysteine. It is also worth noting that over 90% (by weight) of the sulfur-containing compounds identified from the degradation of cysteine contained nitrogen atoms. In contrast, only 9% of heterocyclic compounds from the degradation of glutathione contained both nitrogen and sulfur atoms and all of them were thiazoles. This indicates that glutathione releases hydrogen sulfide more easily than ammonia.

Glutathione, which occurs in the cell of all higher organisms, rapidly evolves hydrogen sulfide as it is heated (Ohloff et al., 1985). The cysteine of muscle protein serves as a precursor for hydrogen sulfide in meat when heating is prolonged (Mecchi et al., 1964). In a glutathione degradation system, the release of hydrogen sulfide and its subsequent reaction with other components generated a large amount of sulfides. Ammonia was released too slowly to generate any nitrogen-containing cyclic sulfides such as alkyl-1,3,5-dithiazines and alkyl-1,3,5-thiadiazines. Two major compounds identified in glutathione degradation were the syn and anti isomers of 3,5-dimethyl-1,2,4-trithiolanes. These accounted for 63.2% of the total volatiles. On the other hand, cysteine degradation yielded a large amount of hydrogen sulfide and ammonia interaction products. 2,4,6-Trimethylperhydro-1,3,5-thiadiazine and 2,4,6-trimethylperhydro-1,3,5-dithiazine, which accounted for 70.9% of the total volatiles, are typical interaction products of acetaldehyde, hydrogen sulfide, and ammonia.

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Registry No. Thiophene, 110-02-1; thiazole, 288-47-1; pyrrole, 109-97-7; 2-methylthiazole, 3581-87-1; 4-methylthiazole, 693-95-8; 2-methylpyridine, 109-06-8; 5-methylthiazole, 3581-89-3; 2-methyl-1,3-dithiolane, 5616-51-3; 2-acetylthiazole, 24295-03-2; 2-methyl-5-ethylthiazole, 19961-52-5; 2,4,6-trimethylperhydro-1,3,5-oxathiazine, 115421-50-6; 3-methyl-2-formylthiophene, 5834-16-2; 2,4,6-trimethylperhydro-1,3,5-thiadiazine, 53897-63-5; 2-(1-oxopropyl)thiazole, 43039-98-1; 3,5-dimethyl-1,2,4-trithiolane, 23654-92-4; 4,6-dimethylperhydro-1,2,3,5-trithiazine, 115421-51-7; 2,4,6-trimethylperhydro-1,3,5-dithiazine, 86241-90-9; 3-methyl-1,2,4-trithiane, 43040-01-3; 2,4-dimethyl-6-ethylperhydro-1,3,5-dithiazine, 54717-13-4; 2,4,6-trimethyl-1,3,5-trithiane, 2765-04-0; 3,6-dimethyl-1,2,4,5-tetrathiane, 67411-27-2; 4,6-dimethyl-1,2,3,5-tetrathiane, 96504-25-5; 1,2,5-trithiepane, 6576-93-8;

3,5,7-trimethyl-1,2,4,6-tetrathiepane, 115421-49-3; 4,7-dimethyl-1,2,3,5,6-pentathiepane, 101517-94-6.

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Original Composition of Marjoram Flavor and Its Changes during Processing

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The composition of monoterpenes in essential oils or flavor extracts from marjoram (*Majorana hortensis* Moench) depends on the method applied for their isolation. Experiments with solvent extracts, with leaf material ground under liquid nitrogen, and with direct injections of the content of oil glands revealed the presence of a common precursor structure. The study of rearrangement reactions of sabinene hydrate and sabinene hydrate acetate confirmed that the sabinene hydrate skeleton represents the primary monoterpene structure in marjoram. Two activated forms are responsible for the formation of rearranged monoterpenes during workup of the plant material: a "bound" form, presumably (*Z*)-sabinene hydrate pyrophosphate, and a "free" form, (*Z*)-sabinene hydrate acetate, which is the main component in the oil glands together with (*Z*)-sabinene hydrate.

Marjoram is a spice plant used because of its content of so-called "essential oil". In the food industry the distilled oil frequently comes to application, on account of

the greater storage stability, the missing microbial contamination, and the known content of individual compounds. The term essential oil implicates by definition the method of preparation, namely the separation of steam-volatile substances by distillation at atmospheric pressure.

The usual gas chromatographic analysis of flavor compounds of such herbs or spices mostly starts with the

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