

methyl-5-ethylthiazole, 19961-52-5; 2-acetylthiophene, 88-15-3; 3-acetylthiophene, 1468-83-3; ethyl disulfide, 110-81-6; ethyl trisulfide, 3600-24-6; ethyl 1-(ethylthio)ethyl disulfide, 94944-48-6; ethyl 1-(ethylthio)ethyl trisulfide, 94944-49-7; ethyl butyl disulfide, 63986-03-8; ethyl 1-(ethylthio)ethyl tetrasulfide, 94944-50-0; ethyl 1-mercaptoethyl sulfide, 31331-54-1; 3,5-dimethyl-1,2,4-trithiolane, 23654-92-4; 2-methyl-1,3-dithiolane, 5616-51-3; 3-methyl-1,2,4-trithiane, 43040-01-3; 3,6-dimethyl-1,2,4,5-tetrathiane, 67411-27-2; γ -thiobutyrolactone, 1003-10-7; 3-methyl-1,2-dithiolane, 55487-20-2; 2,4,6-trimethyl-1,3,5-trithiane, 2765-04-0; 4-methyl-1,2-dithiole-3-thione, 3354-41-4; 5-methyl-1,2-dithiole-3-thione, 3354-40-3; acetaldehyde, 75-07-0; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; 2-pentanone, 107-87-9; 3-hexanone, 589-38-8; 3-methylcyclopentanone, 1757-42-2; 2,3-pentanedione, 600-14-6; 2-acetylpyrrole, 1072-83-9; pyrrole, 109-97-7; *N*-acetylpyrrole, 609-41-6.

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pH Effect on the Volatile Components in the Thermal Degradation of Cysteine

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The pH effect on the volatile components in the thermal degradation of cysteine was studied at pH's 2.2, 5.1, and 7.1, representing the pH values below, around, and above the isoelectric point of cysteine, with a Parr bomb model system. A vigorous degradation occurred at pH 5.1 and a very mild one at pH 7.1. At pH 2.2 the major components formed are 1,2,3-trithia-5-cycloheptene and 2-thiophenethiol. The trithiacycloheptene compound was evaluated as roasted onion and roasted meat odor and was found for the first time in a model system. The mechanism of formation of these two major compounds is proposed. At pH's 5.1 and 7.1, 3,5-dimethyl-1,2,4-trithiolanes possessing a roasted odor are the major components.

INTRODUCTION

Cysteine and other sulfur-containing amino acids are considered important contributions to the formation of various food flavors, especially meat flavor (Hurrell, 1982;

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Ching, 1979; Fujimaki et al., 1969; Kato et al., 1973). Thermal degradation of cysteine was reported by several researchers. Obata and Tanaka (1965) photolyzed cysteine in aqueous medium and found several primary degradation volatiles such as H₂S, NH₃, CO₂, and acetaldehyde. Fujimaki et al. (1969) and Kato et al. (1973) pyrolyzed cysteine at 270-300 °C with no medium and identified additional volatile compounds including amines, thiazolidine, thiazoles, pyridines, and thiophenes. Ledl and Severin (1973) and Ledl (1976) heated cysteine in tributyrin at 150 °C and in soybean oil at 200 °C, respectively. They identified many volatile heterocycles including various types of sulfur-containing compounds. Patterson et al. (1976) pyrolyzed cysteine at higher temperature (850 °C) with no medium and found the most volatile compounds

Table 1. Volatile Components Identified from the Degradation of Cystine at Different pH's^a

compd ID	pH 2.2			pH 5.1			pH 7.1			MS ref or m/e (rel intens)
	OV-1	CWX	GC area %	OV-1	CWX	GC area %	OV-1	CWX	GC area %	
	1	2	T	1	2	T	1	1	5.2	
acetone						55.8				Ten Noever de Brauw et al. (1983)
methyl ethyl ketone	1	2	T	2	2	T	1	1	5.2	Ten Noever de Brauw et al. (1983)
thiophene	2	3	T							Ten Noever de Brauw et al. (1983)
cyclohexene	3	1	8.4	3		1.7	2		3.4	Ten Noever de Brauw et al. (1983)
thiazole	4	5	T	4	3	T	3		T	Ten Noever de Brauw et al. (1983)
2-methylthiazole	5	4	1.4				4		T	Ten Noever de Brauw et al. (1983)
1-mercapto-2-butanone	6		T				5	4	1.7	57 (100), 29 (73), 47 (32), 104 (25), 43 (17)
4,5-dihydro-3(H)-thiophenone	7	10	1.3				6		1.3	Stoll et al. (1967)
2-thiophenethiol	9	11	14.1							API
3-thiophenethiol	10		T							MSDC
2-methyl-1,3-dithiolane	11	8	T							Ledl and Severin (1973)
2-methyl-5-ethylthiazole	12	6	1.2	5	4	T	3		T	Ten Noever de Brauw et al. (1983)
3-methyl-1,2-dithiolane	13	9	T							55 (100), 120 (33), 29 (12), 41 (11), 64 (10)
3-methyl-1,2-dithiolan-4-one	14		T							60 (100), 134 (89), 92 (60), 64 (56), 45 (43), 59 (34)
2-acetylthiophene	15	14	T				7	11	3.6	Ten Noever de Brauw et al. (1983)
3-methylthiophene-2-carboxaldehyde	16	15	1.3	6	7	T	8	12	1.5	Mussinan and Walradt (1974)
2-thiazolyl ethyl ketone	17	12	2.4				9	9	8.0	112 (100), 113 (88), 57 (77), 29 (43), 85 (25), 58 (23)
3,5-dimethyl-1,2,4-trithiolane	18	13	3.1	7	5	13.1	10	5	14.1	Ten Noever de Brauw et al. (1983)
3,5-dimethyl-1,2,4-trithiolane	19	16	3.7	8	6	3.0	11	6	14.2	Ten Noever de Brauw et al. (1983)
thienothiophene				9	8	2.7	12	16	4.0	Gautschi et al. (1967)
3-methyl-1,2,4-trithiane	20	17	34.4				13	15	6.3	Kleipool and Tas (1974)
1,2,3-trithia-5-cycloheptene	21		T	10		2.9	14		1.8	150 (100), 45 (84), 103 (82), 85 (49), 59 (48), 58 (45)
3,6-dimethyl-1,2,4,5-tetrathiane	22		T							Nixon et al. (1979)
3,6-dimethyl-1,2,4,5-tetrathiane										Nixon et al. (1979)
2-acetylthiazole										Ten Noever de Brauw et al. (1983)
5-methylthiophene-2-carboxaldehyde	8	7	2.1							Mussinan and Walradt (1974)
2,4,6-trimethyl-1,3,5-dithiazine										Boelens et al. (1974)
unknown 1, M _r 118										
unknown 2, M _r 180										
unknown 3, M _r 180										
methylene chloride (solvent)	S	S		S	S		S	S		

^aT = trace, less than 1%.

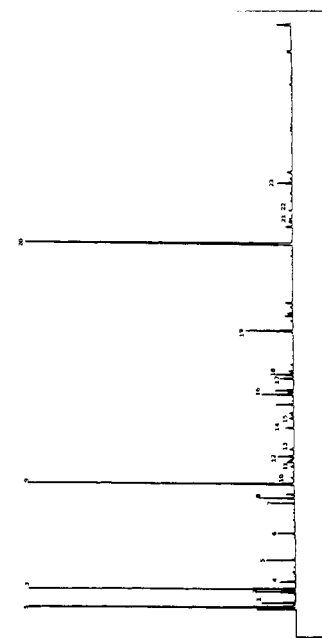


Figure 1. The GC profile of the volatiles from the degradation of Cysteine at pH 2.2 (OV-1 Column). Column: OV-1 fused silica capillary (50 m x 0.32 mm). Temperature: 50-225 °C programmed at 2 °C/min. Detector: flame ionization.

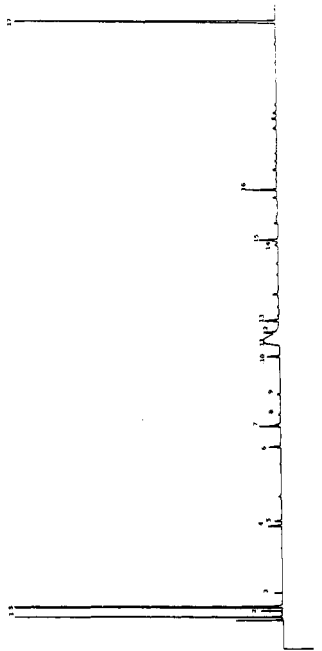


Figure 2. The GC profile of the volatiles from the degradation of cysteine at pH 7.1 (CWX column). Column: Carbowax 20M, fused silica capillary (50 m x 0.32 mm). Temperature: 50-225 °C programmed at 2 °C/min. Detector: flame ionization.

identified were non-sulfur containing. However, literature information pertaining to the pH effect on the volatile components in the thermal degradation of cysteine was very limited. Recently, Shu et al. (1985) reported the thermal degradation of cystine at pH 2.3 and pH 5.5. The volatile profiles were found to be highly pH dependent. One striking difference observed was that 1,2,4-trithiolanes possessing the roasting character were favorably formed over 55% at pH 2.3 but only 6.6% at pH 5.5. As pH value plays a very important role in the chemistry of amino acids, the formation of the degradation products may be influenced by the pH values. Understanding such effects becomes essential for controlling reactions where cysteine is involved.

In this study, cysteine was thermally degraded (160 °C) at pH 2.1, 5.1, and 7.1 representing the pH values below, around, and above the isoelectric point (pI) of cysteine, respectively. The volatile components identified at each pH level are presented and discussed.

EXPERIMENTAL SECTION

As described previously (Shu et al., 1985), each solution was prepared by dissolving 0.05 mol of L-cysteine hydrochloride monohydrate (Ajinomoto Co., Tokyo, Japan) in approximately 450 mL of distilled water, followed by titration to the appropriate pH value (2.1, 5.1, or 7.1) with 10% Na₂CO₃ and, finally, dilution to a total of 500 g with distilled water. The solution was then placed in a 2-L Parr bomb (Parr Instrument Co., Moline, IL) and heated for 1/2 h. The reaction mass obtained was subjected to vacuum steam distillation, extraction, and concentration in that order and the concentrate analyzed by gas chromatography-mass spectrometry (GC-MS). Individual unknown components were isolated by GC and analyzed by proton nuclear magnetic resonance (NMR).

RESULTS AND DISCUSSION

The yield of the volatiles obtained from the degradation of 0.05 mol of cysteine HCl·H₂O at pH 2.2 was 48 mg. The GC profiles on OV-1 and Carbowax 20M (CWX) columns are shown in Figures 1 and 2, respectively. The peaks identified are numbered and the peaks not identified are not numbered. The components identified from this sample along with the peak identification numbers, quantitative data, and the mass spectrum references are compiled in Table I. Except 1,2,3-trithia-5-cycloheptene, all of the components were identified by GC-MS.

The results indicate that at pH 2.2 cyclic sulfides containing five-, six-, and seven-membered rings and thiophenes were mainly formed. In this case, fewer thiazoles were formed, as compared with the degradation of cystine at this pH (Shu et al., 1985).

Of the components identified at pH 2.2 our attention was drawn to peak no. 20 (OV-1), being the component present in largest concentration. The component was subsequently trapped for spectral analyses. The mass spectrum of this compound is shown in Figure 3. The base peak appeared at *m/e* 150 and isotope ratios (*m/e* 152, 13%) indicated three sulfur atoms in the structure. Fragment *m/e* 103 could be due to (M - S-CH₃), and *m/e* 45 due to S=CH⁺. The proton NMR spectrum (Figure 4) was not first order, generally resembling an ABXX' pattern. The splitting pattern shows a multiplet (d and d, apparent splittings of 10 Hz and 2.5 Hz) centered at 3.5 δ, a multiplet (d and d, apparent splitting of 10 Hz and 2.0 Hz) centered at 3.64 δ, and another multiplet at 5.37 δ suggesting 1,2,3-trithia-5-cycloheptene (*M*, 150). The unexpected complexity of the NMR spectrum prompted a search of the literature for related compounds. The

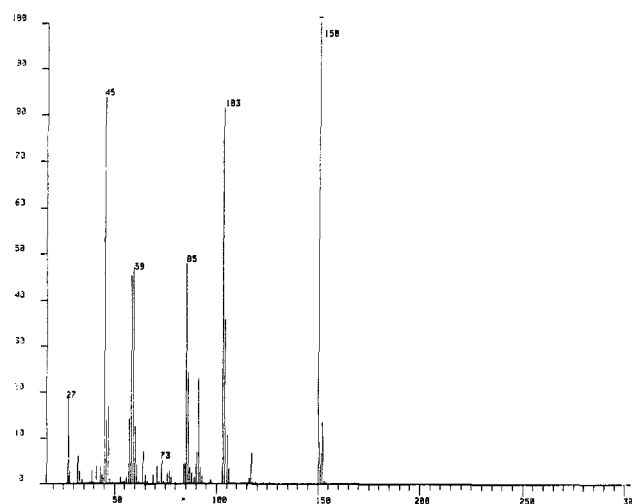


Figure 3. Mass spectrum of peak no. 20 from OV-1 column.

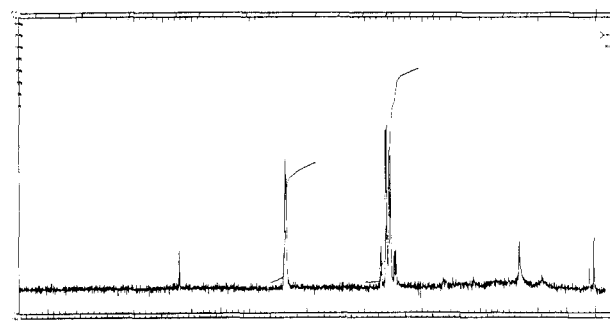


Figure 4. Proton NMR spectrum of peak no. 20 from OV-1 column.

nonequivalence of the methylene protons in this system in the room temperature NMR was confirmed by Friebolin and Kabuss (1965). Therefore the structure was identified as 1,2,3-trithia-5-cycloheptene.

This compound had not been reported in natural food nor in a model system. The odor of this compound from the GC trap was described as roasted onion and roasted meat.

The formation mechanism of 1,2,3-trithia-5-cycloheptene is postulated as shown in Figure 5. It is well-known that cysteine can be degraded into mercaptoacetaldehyde via decarboxylation and deamination (Lien and Nawar, 1974; de Rijke et al., 1981) and to acetaldehyde via rearrangement and decarboxylation (Boelens et al., 1975). Interaction between these compounds results in 1,2,3-trithia-5-cycloheptene.

The other major component found at pH 2.2 was 2-thiophenethiol (14%). The formation mechanism of this component as well as its isomer, 3-thiophenethiol, is proposed in Figure 6. The primary degradation product, mercaptoacetaldehyde, could undergo self-condensation to an intermediate, 2,4-dihydroxy-3-mercaptopenthydrothiophene (aldol condensation and hemithioacetal formation), which could, in turn, lead to the thiophene isomers by dehydration and loss of H₂S.

When the thermal degradation occurred at pH 5.1 (pI), the yield of the volatiles was 202 mg. The GC profiles of the degradation are presented in Figures 7 and 8. The components identified are shown in Table I. The volatile mixture was simple. The acetone peak comprised over 50% of the volatiles. The experiment was repeated and the results confirmed. In addition to acetone, 3,5-dimethyl-1,2,4-trithiolanes were found in significant amounts. Comparison of the degradation of cysteine at

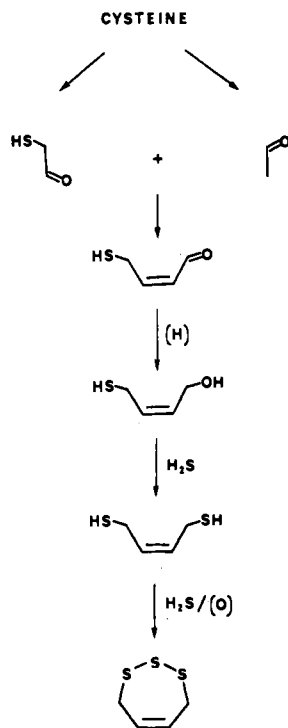


Figure 5. Postulated mechanism of the formation of 1,2,3-trithia-5-cycloheptene.

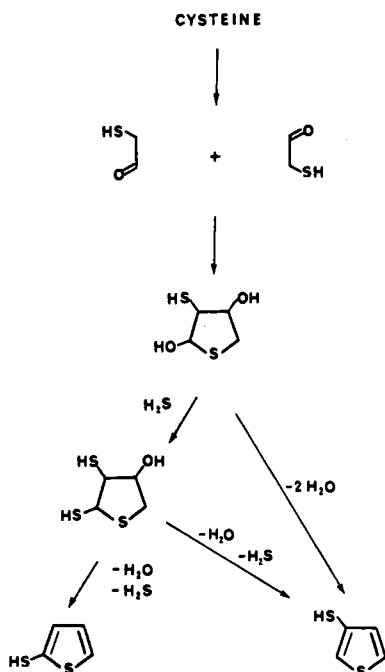


Figure 6. The possible formation of thiophenethiols from cysteine.

pH 2.2 and at pH 5.1 indicates that the formation of 3,5-dimethyl-1,2,4-trithiolanes occurred more readily at pH = *pI* than at pH < *pI*; it is interesting to note that this is the opposite for that reported in thermal degradation of cystine (Shu et al., 1985). This phenomenon could be related to the stability of the disulfide bond of cystine at different pH's.

At pH 7.1 the yield of volatile was only 18 mg. The GC profiles are shown in Figures 9 and 10 and Table I lists the components identified. It is obvious that all of the compounds identified were cyclized compounds except methyl ethyl ketone. The major components were 3,5-dimethyl-1,2,4-trithiolanes, 2-thiazolyl ethyl ketone, and 3-methyl-1,2,4-trithiane. The low yield of volatiles was

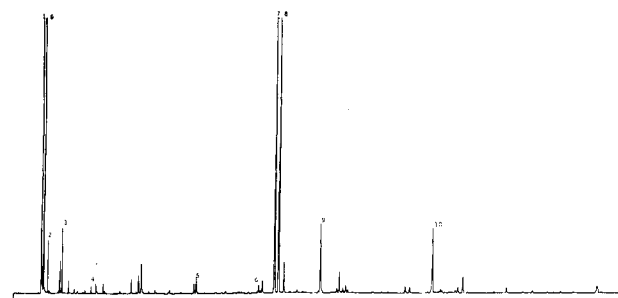


Figure 7. The GC profile of the volatiles from the degradation of cysteine at pH 5.1 (OV-1 column). Column: OV-1, fused silica capillary (50 m × 0.32 mm). Temperature: 50–225 °C programmed at 2 °C/min. Detector: flame ionization.

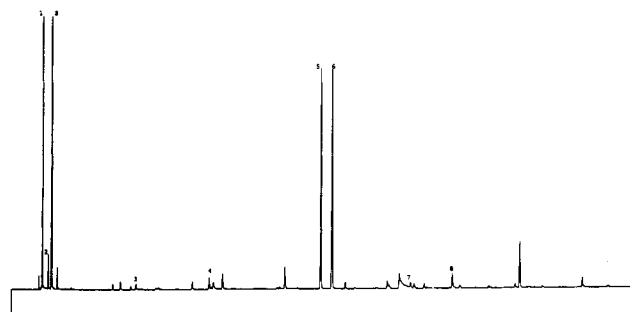


Figure 8. The GC profile of the volatiles from the degradation of cysteine at pH 5.1 (CWX column). Column: carbowax 20M, fused silica capillary (50 m × 0.32 mm). Temperature: 50–225 °C programmed at 2 °C/min. Detector: flame ionization.

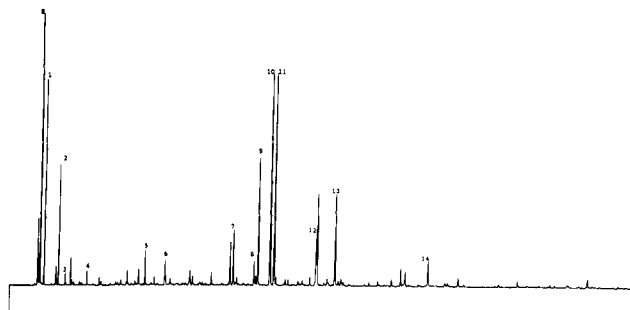


Figure 9. The GC profile of the volatiles from the degradation of cysteine at pH 7.1 (OV-1 column). Column: OV-1, fused silica capillary (50 m × 0.32 mm). Temperature: 50–225 °C programmed at 2 °C/min. Detector: flame ionization.

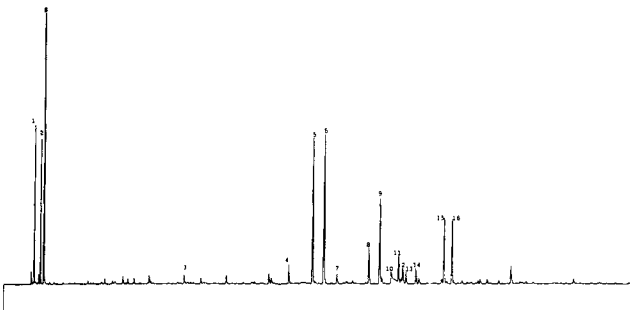


Figure 10. The GC profile of the volatiles from the degradation of cysteine at pH 7.1 (CWX column). Column: Carbowax 20M, fused silica capillary (50 m × 0.32 mm). Temperature: 50–225 °C programmed at 2 °C/min. Detector: flame ionization.

evidence of a mild degradation taking place at pH 7.1.

In summary, this study has revealed that at pH *pI* the degradation of cysteine is very vigorous and at pH > *pI* very mild. Degradation of cysteine favors formation of 1,2,3-trithia-5-cycloheptene at pH < *pI* and favors for-

mation of 3,5-dimethyl-1,2,4-trithiolanes at pH = pI.

ACKNOWLEDGMENT

We are indebted to Dr. Manfred Vock for his organoleptic evaluation in this study.

Registry No. Acetone, 67-64-1; methyl ethyl ketone, 78-93-3; thiophene, 110-02-1; cyclohexene, 110-83-8; thiazole, 288-47-1; 2-methylthiazole, 3581-87-1; 1-mercapto-2-butanone, 39861-37-5; 4,5-dihydro-3(2*H*)-thiophene, 1003-04-9; 2-thiophenethiol, 7774-74-5; 3-thiophenethiol, 7774-73-4; 2-methyl-1,3-dithiolane, 5616-51-3; 2-methyl-5-ethylthiazole, 19961-52-5; 3-methyl-1,2-dithiolane, 55487-20-2; 3-methyl-1,2-dithiolan-4-one, 72771-03-0; 2-acetylthiophene, 88-15-3; 3-methylthiophene-2-carboxaldehyde, 5834-16-2; 2-thiazolyl ethyl ketone, 43039-98-1; 3,5-dimethyl-1,2,4-trithiolane, 23654-92-4; 3-methyl-1,2,4-trithiane, 43040-01-3; 1,2,3-trithia-5-cycloheptene, 13005-82-8; 3,6-dimethyl-1,2,4,5-tetrathiane, 67411-27-2; 2-acetylthiazole, 24295-03-2; 5-methylthiophene-2-carboxaldehyde, 13679-70-4; 2,4,6-trimethyl-1,3,5-dithiazine, 94944-51-1; cysteine, 52-90-4.

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Volatile Components of the Thermal Degradation of 2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone

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2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone or DMHF was subjected to a roasting temperature of 160 °C for 30 min in a closed system at various pH values (2.2, 5.1, and 7.1). The yield of the total volatiles generated decreased with increasing pH value, indicating that degradations occurred more readily at a lower pH. Generally, the volatiles identified were acyclic carbonyls and 3(2*H*)-furanone derivatives, with furanone production favored at the higher pH values. Formation of the described products implies that during thermal degradations in water, DMHF undergoes ring opening and hydrolysis first, then, by a retroaldolization, produces the primary degradation products which react in an intermolecular fashion to form the secondary products. Possible formation mechanisms for the products are postulated.

INTRODUCTION

2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone or DMHF has been described as being "burnt pineapple" like and the major "character impact" compound of pineapple flavor concentrate (Rodin et al., 1965). In the flavor industry, this compound is very important due to its pleasant or-

ganoleptic character and has been used extensively for flavoring jams, jellies, beverages, ice creams, alcoholic drinks, and sweets (Hirvi et al., 1980).

DMHF was found in pineapple (Rodin et al., 1965), strawberries (Re et al., 1973), beef broth (Tonsbeek et al., 1968), and roasted almonds (Takei and Yamanishi, 1974) and was also characterized in various model systems such as the degradation of fructose (Shaw et al., 1968), the pyrolysis of D-glucose (Fagerson, 1969; Heyns et al., 1966; Johnson et al., 1969), pyrolysis of 1-deoxy-1-piperidino-D-fructose (Mills et al., 1969), roasting of alanine and rhamnose (Shaw and Berry, 1977), and reactions between rhamnose and piperidinyl acetate (Hodge and Fisher, 1963).

Reports on the stability of DMHF were limited. Hodge et al. (1963) observed that at 25 °C DMHF was very unstable in air and in aqueous solutions. Recently Hirvi

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