

## Formation of Oxazolines and Oxazoles in Strecker Degradation of DL-Alanine and L-Cysteine with 2,3-Butanedione

2,4,5-Trimethyl-3-oxazoline and 2,4,5-trimethyloxazole were identified in the reaction mixture of DL-alanine and 2,3-butanedione. 2,4,5-Trimethyloxazole and 4,5-dimethyloxazole were identified in the reaction mixture of L-cysteine and 2,3-butanedione. Plausible mechanisms are proposed for the formation of these oxazoles and oxazolines.

Oxazoles and oxazolines have recently been receiving increased attention in food flavor research (Maga, 1978, 1981). Oxazoles and oxazolines have been reported only in food systems which have undergone moderate heating. Both classes of oxygen- and nitrogen-containing heterocycles possess potent sensory qualities at low concentrations.

The occurrence of oxazoles has been reported in cocoa (Vitzthum et al., 1975), coffee (Stoffelsma et al., 1968), meat products (Chang and Peterson, 1977), roasted barley (Harding et al., 1978), baked potato (Coleman et al., 1981), and roasted peanuts (Lee et al., 1981). Oxazoles have also been reported in various model systems, namely, furfural, hydrogen sulfide, and ammonia (Shibamoto, 1977), rhamnose and ammonia (Shibamoto and Bernhard, 1978), D-glucose and ammonia (Shibamoto et al., 1979), and maltol and ammonia (Shibamoto et al., 1981). Ho and Tuorto (1981) reported the synthesis and sensory properties of 15 4,5-dialkyloxazoles.

The first oxazoline, 2,4,5-trimethyl-3-oxazoline, was reported by Chang et al. (1968) in the volatiles of boiled beef. Mussinan et al. (1976) identified oxazolines but no oxazoles in their beef system. Peterson et al. (1975) reported that in the volatiles of canned beef stew, both 2,4,5-trimethyloxazole and 2,4,5-trimethyl-3-oxazoline were present and the relative size of the gas chromatographic peak associated with 2,4,5-trimethyloxazole was medium whereas that for 2,4,5-trimethyl-3-oxazoline was extra large. Lee et al. (1981) identified 2-methyl-3-oxazoline, 2,4-dimethyl-3-oxazoline, and 2,4,5-trimethyl-3-oxazoline in the volatile flavor of roasted peanuts. Mussinan et al. (1976) have suggested that 2,4,5-trimethyl-3-oxazoline can form in heated meat systems by the thermal interaction and rearrangement of the compounds ammonia, acetaldehyde, and acetoin. Rizzi (1969) identified the 2-isopropyl-4,5-dimethyl-3-oxazoline in the Strecker degradation of DL-valine with 2,3-butanedione.

In an attempt to identify the source of 2,4,5-trimethyl-3-oxazoline and 2,4,5-trimethyloxazole, which were found in the volatiles of meat and roast peanuts, this paper reports the reactions of 2,3-butanedione and alanine or cysteine.

### EXPERIMENTAL SECTION

**Reaction of DL-Alanine and 2,3-Butanedione.** A mixture containing 13.35 g of reagent-grade DL-alanine (0.150 mol), 12 mL of redistilled 2,3-butanedione (0.137 mol), and 50 mL of freshly redistilled diglyme was stirred and refluxed for 45 min. The cooled reaction mixture was steam distilled. The 300 mL of pale yellow distillate obtained was saturated with NaCl and extracted 3 times with ethyl ether. The ether extract was dried over anhydrous sodium sulfate and concentrated to 10 mL on a 15-plate Oldershaw column.

**Reaction of L-Cysteine and 2,3-Butanedione.** A mixture containing 9.08 g of L-cysteine (0.075 mol), 6 mL

of 2,3-butanedione (0.069 mol), and 25 mL of diglyme was reacted and treated in the same manner as described under Reaction of DL-Alanine and 2,3-Butanedione.

**Fractionation of the Reaction Mixtures.** The reaction mixtures obtained were fractionated on a Beckman GC-55 gas chromatograph equipped with a flame ionization detector, fitted with a 2 mm i.d.  $\times$  3 m stainless steel column packed with 10% SP-1000 on 60-80-mesh Chromosorb W. The flow rate was 30 mL/min with a column temperature programmed from 40 to 250 °C at a rate of 10 °C/min. Each peak was successively collected for GC-mass analysis by trapping the exit port gases in dry ice cooled glass capillary traps.

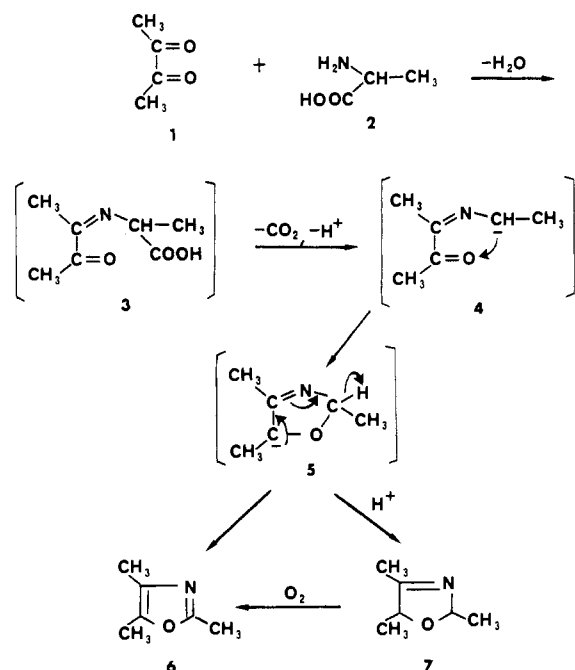
**Identification of Gas Chromatographic Fractions.** A Du Pont 21-490 mass spectrometer with a jet separator interfaced to a Varian Moduline 2700 gas chromatograph, fitted with an FID detector and a 2 mm i.d.  $\times$  3 m glass column packed with 10% OV-101 on 60-80-mesh Chromosorb W, was used for GC-mass determination. The flow rate was 30 mL/min with the column temperature programmed from 50 to 250 °C at rate of 10 °C/min.

### RESULTS AND DISCUSSION

In an attempt to explain the source of 2,4,5-trimethyl-3-oxazoline in the flavor of meat (Chang et al., 1968; Mussinan et al., 1976) and roasted peanuts (Lee et al., 1981), DL-alanine was reacted with 2,3-butanedione at roasting temperature (162 °C), and the reaction mixture was fractionated by gas chromatography and analyzed by GC-mass spectrometry. The major product was tetramethylpyrazine. The mechanism for the formation of tetramethylpyrazine in the reaction of 2,3-butanedione and amino acids has been suggested by Rizzi (1969). Both 2,4,5-trimethyl-3-oxazoline and 2,4,5-trimethyloxazole were found in the reaction mixture in a ratio of 0.23 to 1.

A plausible explanation for the formation of 2,4,5-trimethyloxazole and 2,4,5-trimethyl-3-oxazoline from DL-alanine and 2,3-butanedione is shown in Figure 1. Initially 1 and 2 react with elimination of water to form a thermally unstable Schiff base 3 (Schönberg et al., 1948). Decarboxylation of 3 leads to an anion 4 which can cyclize to the 3-oxazolinide ion 5. Protonation of 5 results in the formation of 2,4,5-trimethyl-3-oxazoline. 2,4,5-Trimethyloxazole could have been formed either by the oxidation of 2,4,5-trimethyl-3-oxazoline or by the loss of the hydride ion from 5. In previous work, Rizzi (1969) identified 2-isopropyl-3-oxazoline but no 2-isopropylloxazole in the reaction of DL-valine and 2,3-butanedione. A probable cause for the absence of oxazole was that the reaction was carried out under nitrogen.

In the reaction mixture of L-cysteine with 2,3-butanedione, aside from tetramethylpyrazine, 2,4,5-trimethyloxazole and 4,5-dimethyloxazole were identified in a ratio of 1 to 0.75. No sulfur-containing oxazole or oxazoline could be detected. A plausible mechanism for this reaction is shown in Figure 2. Apparently, in the cyclic oxazolinide



**Figure 1.** Formation of 2,4,5-trimethyloxazole and 2,4,5-trimethyl-3-oxazoline from the reaction of DL-alanine and 2,3-butanedione.

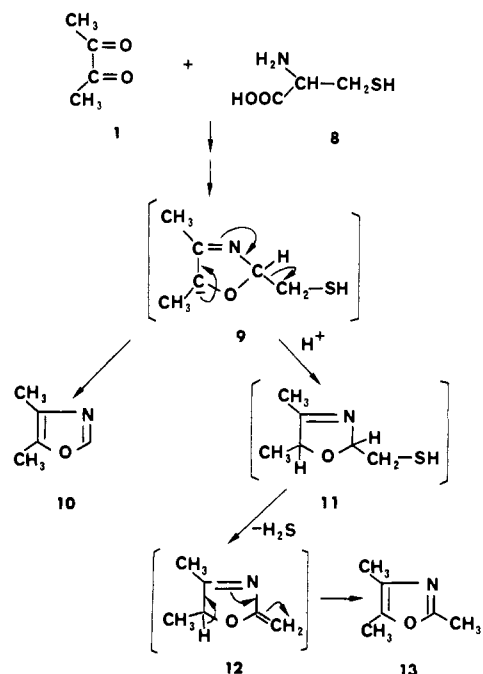
ion 9, the lability of the -CH<sub>2</sub>SH side chain results in its cleavage and aromatization to the 4,5-dimethyloxazole. The formation of 2,4,5-trimethyloxazole may be due to the loss of H<sub>2</sub>S from oxazoline, 11, followed by tautomerism of 12.

#### ACKNOWLEDGMENT

We thank Joan B. Shumsky for her secretarial aid.

#### LITERATURE CITED

- Chang, S. S.; Hirai, C.; Reddy, B. R.; Herz, K. O.; Kato, A.; Sipma, G. *Chem. Ind. (London)* **1968**, 1639.  
 Chang, S. S.; Peterson, R. J. *J. Food Sci.* **1977**, *42*, 298.  
 Coleman, E. C.; Ho, C.-T.; Chang, S. S. *J. Agric. Food Chem.* **1981**, *29*, 42.  
 Harding, R. J.; Wren, J. J.; Nursten, H. E. *J. Inst. Brew.* **1978**, *84*, 41.  
 Ho, C.-T.; Tuorto, R. M. *J. Agric. Food Chem.* **1981**, *29*, 1306.  
 Lee, M.-H.; Ho, C.-T.; Chang, S. S. *J. Agric. Food Chem.* **1981**, *29*, 684.  
 Maga, J. A. *J. Agric. Food Chem.* **1978**, *26*, 1049.  
 Maga, J. A. *CRC Crit. Rev. Food Sci. Nutr.* **1981**, *12*, 295.  
 Mussinan, C. J.; Wilson, R. A.; Katz, I.; Hruza, A.; Vock, M. H. *ACS Symp. Ser.* **1976**, No. 26, 133.  
 Peterson, R. J.; Izzo, H. J.; Jungermann, E.; Chang, S. S. *J. Food Sci.* **1975**, *40*, 948.  
 Rizzi, G. P. *J. Org. Chem.* **1969**, *34*, 2002.



**Figure 2.** Formation of 2,4,5-trimethyloxazole and 4,5-dimethyloxazole from the reaction of L-cysteine and 2,3-butanedione.

Schönberg, A.; Moubacher, R.; Mostafa, A. *J. Chem. Soc.* **1948**, 176.

Shibamoto, T. *J. Agric. Food Chem.* **1977**, *25*, 206.

Shibamoto, T.; Akiyama, T.; Sakaguchi, M.; Enomoto, Y.; Masuda, H. *J. Agric. Food Chem.* **1979**, *27*, 1027.

Shibamoto, T.; Bernhard, R. A. *J. Agric. Food Chem.* **1978**, *26*, 183.

Shibamoto, T.; Nishimura, O.; Mihara, S. *J. Agric. Food Chem.* **1981**, *29*, 643.

Stoffelsma, J.; Sipma, G.; Kettenes, D. K.; Pyker, J. *J. Agric. Food Chem.* **1968**, *16*, 1000.

Vitzthum, O. G.; Werkhoff, P.; Hubert, P. *J. Food Sci.* **1975**, *40*, 911.

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Received for review November 9, 1981. Accepted March 19, 1982. This work was performed as a part of NJAES Project No. 10205, supported by the New Jersey Agricultural Experimental Station, Hatch Regional Fund, NE-116. Partial support was received from Rutgers Research Council. Paper of the Journal Series, New Jersey Agricultural Experiment Station, Cook College, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903.