Studies on the Formation and Stability of the Roast-Flavor Compound 2-Acetyl-2-thiazoline

Thomas Hofmann† and Peter Schieberle*,‡

Deutsche Forschungsanstalt für Lebensmittelchemie und Institut für Lebensmittelchemie der Technischen Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany

2-(1-Hydroxyethyl)-4,5-dihydrothiazole (HDT) was identified by ^{1}H- and ^{13}C-NMR measurements as the main volatile product formed by storage of an aqueous solution of cysteamine and methylglyoxal at low temperatures (6 °C). The structure of HDT was confirmed by synthesis. Systematic studies on the thermal stability of the HDT under different conditions either in aqueous solution or during high-resolution gas chromatography revealed that HDT is an important intermediate in the formation of the intensely roasty smelling food flavor compound 2-acetyl-2-thiazoline (AT). Model studies showed that more than 10% of the precursor HDT was converted into AT simply by heating for 10 min in water. The activation energy of this reaction was 57.4 kJ/mol. Experiments on the thermal stability of AT itself revealed that heating in aqueous solution also led to a degradation of AT, whereas heating in an oil significantly stabilized the flavor compound.

Keywords: *2-(1-Hydroxyethyl)-4,5-dihydrothiazole; 2-acetyl-2-thiazoline; flavor precursor; stable isotope dilution analysis*

INTRODUCTION

2-Acetyl-2-thiazoline (AT) has been reported for the first time among food flavors as a volatile constituent of beef broth (Tonsbeek et al., 1971). The compound was later identified in roast beef (Hartmann et al., 1983) and, also, overpasteurized beer (Tressl et al., 1983).

Using aroma extract dilution analysis (AEDA), the flavor compound, eliciting an attractive roasty, popcorn-like odor, has recently been established as a key contributor to several processed meat products, such as chicken broth (Gasser and Grosch, 1990), roast beef (Cerny and Grosch, 1993), stewed beef (Guth and Grosch, 1993), boiled trouts (Milo and Grosch, 1993), and roasted white sesame seeds (Schieberle, 1993). Furthermore, AT was detected among the odor-active volatiles of stewed beef juice (Guth and Grosch, 1994).

Volatile fractions generated by reacting cysteine with carbohydrates exhibit flavors resembling processed beef meat. Investigations on the chemical composition of such fractions have led to the identification of AT among the numerous volatiles generated from such precursor mixtures (Sakaguchi and Shibamoto, 1978; Silwar, 1992). Recent studies applying AEDA on the volatiles formed by the reaction of ribose/cysteine (Hofmann and Schieberle, 1995) have revealed that AT in fact contributes significantly to the roasty odors, and it was concluded that AT is a key odorant of such Maillard-type reaction flavors containing cysteine.

Hayashi and Shibamoto (1985) have reported that AT is formed in relatively high yields by reacting 1-mercapto-2-aminoethane (cysteamine) with 2-oxopropanal (methylglyoxal). This result suggested both compounds are important intermediates in AT formation from cysteine and carbohydrates. On the basis of the fact that at lower temperatures the 2-acetylthiazolidine was predominantly formed, it has been assumed (Hayashi and Shibamoto, 1985) that the flavor compound may be formed by oxidation of this intermediate.

Precursors generating meat-like odorants upon heating are of special interest since they would offer the possibility to enhance the desired flavor *in situ* during cooking.

The following investigation was undertaken to gain a more detailed insight into the intermediates and reaction mechanisms governing the formation of AT from cysteine and carbohydrates and, furthermore, to study the thermal stability of AT.

MATERIALS AND METHODS

Chemicals. 1-Mercapto-2-aminoethane hydrochloride (cysteamine hydrochloride), 2-oxopropanal (methylglyoxal; 40% in water), hydroxypropanoic acid nitrile, and lithium aluminum hydride were obtained commercially (Aldrich, Steinheim, Germany).

Synthesis. *2-(1-Hydroxyethyl)-4,5-dihydrothiazole (HDT).* A mixture of cysteamine hydrochloride (12 mmol), 2-hydroxypropanoic acid nitrile (4 mmol), and ammonium acetate (1 g) in methanol (4 mL) was stirred for 32 h at room temperature. After the addition of water (10 mL), the HDT formed was extracted with diethyl ether (total volume 50 mL), and an aliquot was purified by flash chromatography as detailed in the following: The stationary phase (Bakerbond Diol; 40 μm) was filled 15 cm high into a glass column (35.9 × 1.9 cm; J. T. Baker No. 7022-01) which was equipped with a reservoir (250 mL) and a pressure regulator. The material was then equilibrated by flushing with *n*-pentane/diethyl ether (100 mL, 8 + 2 by vol) under a slight pressure of nitrogen. After application of the concentrated reaction mixture (10 mL) onto the column, elution (6 mL/min) was performed using the following *n*-pentane/diethyl ether mixtures: 180 mL/8 + 2 by vol (fraction A), 180 mL/7 + 3 by vol (fraction B), 150 mL/6 + 4 by vol (fraction C1), 30 mL/6 + 4 by vol (fraction C2), 30 mL/1 + 1 by vol (fraction D1) and another 150 mL/1 + 1 by vol (fraction D2). The 2-(1-hydroxyethyl)-4,5-dihydrothiazole, eluting in fractions C2–D2 (overall yield 61%) was characterized by ^{1}H-NMR (cf. Tables 1 and 2) and mass spectral measurements.

* Author to whom correspondence should be addressed (telephone +49-89-3209-3265; fax +49-89-3209-4183).

† Deutsche Forschungsanstalt für Lebensmittelchemie.

‡ Institut für Lebensmittelchemie der Technischen Universität München.

0021-8561/95/1443-2946$09.00/0

Table 1. Assignment of ^{1}H-NMR Signals (C_6D_6) in Connection with the Structure of HDT in Figure 4

H at carbon	δ	multiplicity	J (Hz)
7	1.38	d, 3H	$J_{7-6} = 6.64$
2	2.56	t, 2H	$J_{2-3} = 8.41$
3	3.73	m, 2H	$J_{3-2} = 8.41$; $J_{3-6} = 1.77$
6	4.50	q, 1H	$J_{6-7} = 6.64$; $J_{6-3} = 1.77$

Table 2. Assignment of ^{13}C-NMR Signals (C_6D_6) in Connection with the Structure of HDT in Figure 4

carbon atom	δ	DEPT analysis	heteronuclear ^{1}H, ^{13}C multiple quantum coherence via ^1J (C, H)
7	22.2	CH_3	3H–C7
2	33.3	CH_2	2H–C2
3	63.6	CH_2	2H–C3
6	67.8	CH	1H–C6
5	178.1	C	

MS/EI: *m/e* (%) 60 (100), 131 (40), 45 (30), 59 (26), 116 (22), 61 (12), 87 (8), 114 (8).

2-Acetyl-2-thiazoline and [^{2}H]$_4$-2-acetyl-2-thiazoline were synthesized as described by Cerny and Grosch (1992, 1993).

Model Reaction. Cysteamine hydrochloride (20 mmol) and methylglyoxal (20 mmol), dissolved in sodium/potassium phosphate buffer (2 L; 0.5 mol/L; pH 7.0), were allowed to react for 18 h at 6 °C. Aliquots (400 mL) were then mixed with methanol/dichlormethane (1.5 L, 2 + 1 by vol), and after the addition of water (500 mL), the combined organic layers were dried over Na_2SO_4. The solution was concentrated at room temperature to about 5 mL with a rotary evaporator, and then the dichloromethane was blown off in a stream of nitrogen. The residue was taken up in *n*-pentane/diethyl ether (500 μL, 8 + 2 by vol) and analyzed by HRGC/MS and HRGC/olfactometry as described recently (Schieberle, 1991).

Isolation and Characterization of a 2-Acetyl-2-thiazoline Precursor. A precursor of AT was isolated from the extract of the cysteamine/2-oxopropanal model mixture by flash chromatography following the procedure reported under Synthesis. The combined fractions C2 and D1 containing the precursor compound were separated by HPLC. The residue was taken up in *n*-pentane/diethyl ether (500 μL), and aliquots (50 μL) were repeatedly injected onto a stainless steel column (25 cm × 0.46 cm) which was filled with a slurry of Lichrospher 100 Diol (Bischoff, Heilbronn, Germany; 5 μm) in *n*-pentane/diethyl ether (3 + 2 by vol). Elution was performed with this solvent mixture (2 mL/min) by means of an HPLC pump (Type 100A; Beckman, Munich, Germany). The effluent was monitored with a refractive index detector (SE-11; Shodex; Erma Optical Works Ltd.). To locate the precursor compound, fractions of 1 mL were collected (elution range 3–15 mL), and aliquots (1 μL) were then injected via a hot injector onto the DB-5 column. The generation of 2-acetyl-2-thiazoline was monitored by HRGC/olfactometry and HRGC/MS. The eluate in the elution range of 4–8 mL containing the precursor was collected, freed from the solvent mixture, and then taken up in benzene-d_6 for NMR measurements.

High-Resolution Gas Chromatography (HRGC)/Mass Spectrometry (MS). HRGC analyses were performed on a gas chromatograph Type 5300 (Fisons, Mainz, Germany) by using the following capillary columns: column DB-5 (30 m × 0.32 mm; J + W Scientific, Fisons Instruments, Mainz, Germany) and column FFAP (30 m × 0.32 mm; free fatty acid phase; J&W, distributed by ANALYT, Müllheim, Germany). For mass spectral measurements the columns were coupled to either a Type 8230 mass spectrometer (Finnigan, Bremen, Germany) or an Incos XL (Finnigan), both running in the electron impact mode at 70 eV (MS/EI). Samples were applied either by using the "cold on-column" technique (GC Type 5300; Fisons Instruments) or via a heated injector equipped with a silylated glass liner (GC/Star 3400 CS; Varian, Darmstadt, Germany).

Quantification of 2-Acetyl-2-thiazoline. At the end of the reaction times detailed in Tables 3–5, the mixtures were cooled to room temperature. After addition of the internal standard [^{2}H]$_4$-2-acetyl-2-thiazoline (dissolved in 1 mL of methanol), the analyte and the internal standard were isolated by extraction with diethyl ether (aqueous mixtures) followed by high-vacuum distillation (for samples in oil) using the apparatus described recently (Guth and Grosch, 1989). In the latter case, the oil was diluted with diethyl ether (30 mL) prior to the distillation procedure to increase the yields of the target compounds. Quantification of AT was performed on capillary column DB-5 by mass chromatography (ion trap detector, ITD 800; Finnigan) and by using chemical ionization with methanol (Cerny and Grosch, 1993).

Table 3. Influence of the Temperature and the Heating Time on the Generation of AT from HDT[a]

heating time (min)	amount of AT[b] (μg) generated at 50 °C	60 °C	75 °C	90 °C	100 °C
1	<0.1	0.2	0.6	1.8	7.3
5	0.3	1.0	2.2	7.2	15.3
10	0.8	1.9	3.8	8.9	16.1
20	1.5	2.6	5.6	10.0	10.3
30	1.8	3.2	7.0	10.3	6.7
60	2.4	4.1	10.0	7.6	1.8

[a] HDT (150 μg) was dissolved in water (10 mL; pH 7.0) and heated. [b] The amounts were determined by running a stable isotope dilution analysis (Cerny and Grosch, 1993). Data are mean values of triplicates.

Table 4. Degradation of AT during Heating[a]

heating time (min)	degradation (%)	heating time (min)	degradation (%)
0	0	20[b]	>99
5	7	20[c]	2.5
10	31		
20	59		
60	96		

[a] 2-Acetyl-2-thiazoline (120 μg) was refluxed in tap water (10 mL). The amounts present after the reaction time were determined by a stable dilution assay (Cerny and Grosch, 1993). Data are mean values of triplicates. [b] The reaction was performed in sodium/potassium phosphate buffer (50 mL; pH 5.0; 0.5 mol/L) at 145 °C in a laboratory autoclave. [c] Heating was performed in sunflower oil at 100 °C.

Table 5. Influence of the pH on the Amount of AT Generated from HDT[a]

expt	pH value	AT[b] (mg)	expt	pH value	AT[b] (mg)
1	3.0	1.8	5	9.0	22.8
2	5.0	4.0	6	7.0[c]	10.3
3	5.6	5.6	7	7.0[d]	13.8
4	7.0	10.2			

[a] HDT (150 μg) was refluxed for 20 min in water (10 mL). The pH value was adjusted with either HCl (1 mol/L) or NaOH (1 mol/L) prior to boiling. [b] Quantification was performed by a stable isotope dilution assay (Cerny and Grosch, 1993). Data are mean values of triplicates. [c] Sodium/potassium phosphate (5 mmol) was added. [d] The reaction was performed in sunflower oil (10 mL).

NMR Spectroscopy. ^{1}H-NMR, ^{13}C-NMR, and ^{13}C-DEPT (distorsionless enhancement by polarization transfer) spectra were recorded in benzene-d_6 (MSD Isotopes, Montreal, Canada) at room temperature by means of an AM 360 (Bruker, Karlsruhe, Germany) as detailed recently (Hofmann et al., 1995). For HMBC (heteronuclear multiple bond correlation) and DQF-COSY spectra an AM 200 (Bruker) was used. The signals were assigned according to tetramethylsilane as the internal standard.

RESULTS

In a solvent extract obtained from an aqueous solution of cysteamine and methylglyoxal, which had been reacted for 18 h at 6 °C, an overall weak odor was detectable.

HRGC analysis of this extract, which had been applied via a hot injector on a DB-5 capillary column,

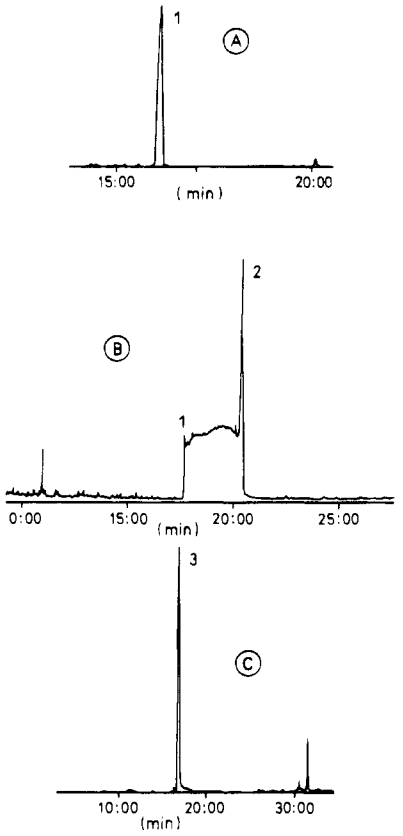

Figure 1. HRGC chromatograms of the reaction products obtained from an aqueous cysteamine/methylglyoxal solution: (A) hot injector/DB-5 capillary column; (B) cold on-column injector/FFAP capillary column; (C) cold on-column injector/DB-5 capillary column. For compounds **1**–**3**, cf. text.

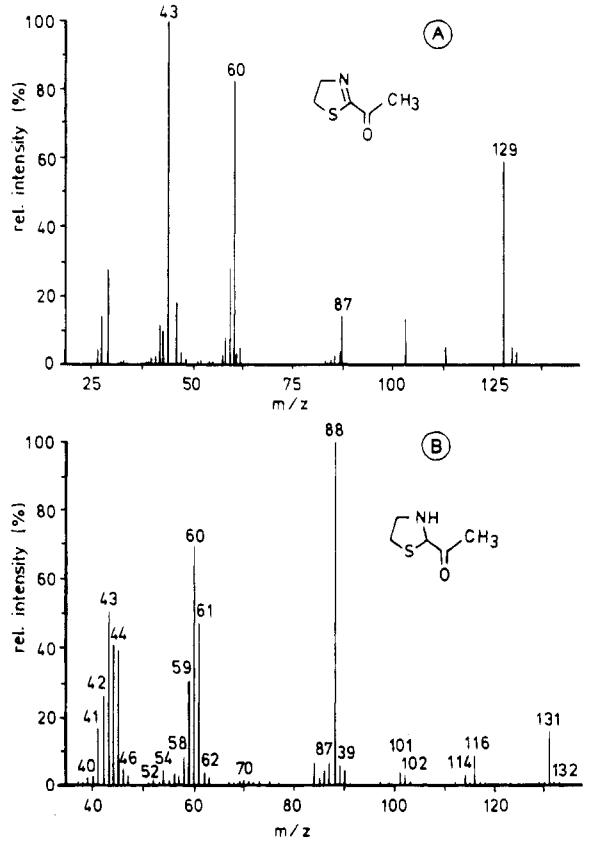

Figure 2. Mass spectra of 2-acetyl-2-thiazoline (A) and 2-acetylthiazolidine (B).

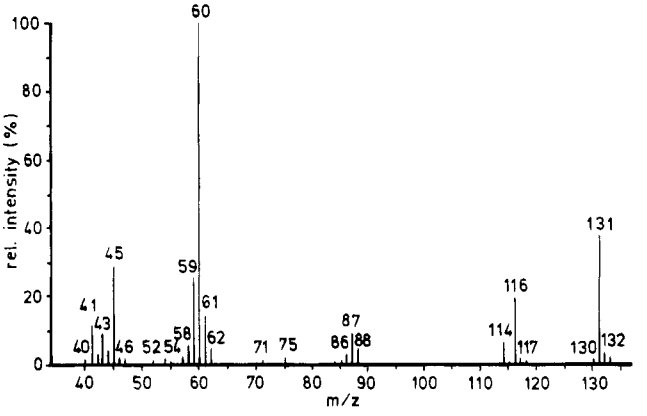

Figure 3. Mass spectrum (MS/EI) of compound **3** isolated from the cysteamine/methylglyoxal solution.

resulted in one single peak (Figure 1A). The compound was identified as 2-acetyl-2-thiazoline (AT) on the basis of its mass spectrum (Figure 2A) and its intense roasty odor detected in the sniffing port. Because the extract exhibited only a very weak odor, we assumed that the AT might be formed by a thermal degradation of an unknown intermediate in the hot injector system.

In a second experiment, the reaction products were applied onto an FFAP column via a cold on-column injector. As indicated in Figure 1B, a broad signal was detectable. In the elution range of peak 1, the mass spectrum of 2-acetyl-2-thiazoline was recorded, whereas in the elution range of peak 2, a mass spectrum (cf. Figure 2B) was obtained, which was in agreement with the key fragment ions published by Sakaguchi and Shibamoto (1985) for 2-acetylthiazolidine. Between the elution of both compounds, the intense roasty odor of the AT was perceivable; however, the mass spectra recorded in this elution range could not be interpreted.

The data suggested that, during HRGC analysis, a degradation reaction takes place, in which the polar stationary HRGC phase might be involved. Therefore, in a third run, the reaction products were applied by the cold on-column technique and separated by HRGC on the nonpolar silicone DB-5 stationary phase. In the chromatogram only one compound was detectable (no. **3**; Figure 1C), showing a retention index on the DB-5 stationary phase ($RI_{DB\text{-}5}$) of 1124, which significantly differed from that of AT ($RI_{DB\text{-}5}$ = 1111) and, also, from that of 2-acetylthiazolidine ($RI_{DB\text{-}5}$ = 1152).

The molecular mass of compound **3** (Figure 3) amounted to 131 (established by MS/CI), which is 2 mass units higher than that of AT (cf. Figure 2A). Because a fragment ion of the thiazoline ring (m/e 87) and an ion, most likely resulting from a subsequent elimination of HCN (*m/e* 60 = *m/e* 87 − 27), were present in compound **3** (Figure 3), a (hydroxyethyl)-dihydrothiazole structure was assumed. This assumption is also corroborated by the ions *m/e* 116 and 114 probably formed by elimination of a methyl group and water, respectively, from the molecular ion.

To clarify its structure, compound **3** was isolated and purified by liquid chromatography and, then, several NMR measurements were performed.

In the ^{1}H-NMR spectrum four signals were detectable. In Table 1, these are assigned according to the proposed structure of 2-(1-hydroxyethyl)-4,5-dihydrothiazole in Figure 4. The signal patterns at carbons 2 and 3 were nearly identical with that obtained for 2-acetyl-2-thiazoline (data not shown). However, the quartet signal for the methine proton at carbon 6, resulting from

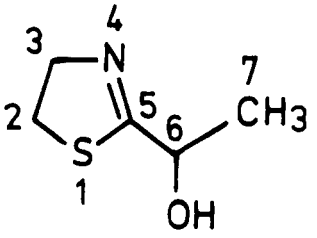

Figure 4. Structure determined for compound **3** as 2-(1-hydroxyethyl)-4,5-dihydrothiazole (HDT).

a coupling with the methyl protons at carbon 7, established a secondary alcohol structure in compound **3**.

Several ^{13}C-NMR experiments (Table 2) and the agreement of the NMR and MS data with the synthesized reference compound confirmed the proposed structure of compound **3** as 2-(1-hydroxyethyl)-4,5-dihydrothiazole (HDT).

To investigate the potency of the HDT as precursor of the AT, the following model experiments were performed. In a first set of experiments, the precursor HDT was heated in aqueous solution, and the amounts of AT liberated under different conditions were quantified by a stable isotope dilution analysis. As shown in Table 3, in the temperature region of 50–75 °C, the amount of AT increased with increasing reaction time from 1 to 60 min. In these experiments, the highest amount of the AT was liberated from HDT after 60 min at 75 °C.

As expected, in the experiments performed at 90 or 100 °C (Table 3), the flavor compound was liberated much more quickly than at the lower reaction temperatures. The highest yield of AT (11%) was obtained when HDT was maintained for 10 min at 100 °C.

However, at these high temperatures, the formation of AT runs through a maximum with a decrease in the concentration after longer reaction times. For example, heating at 100 °C for 60 min only yielded $^1/_{10}$ of the AT found after 10 min. This result suggested that AT is relatively unstable and is degraded to a significant extent during heating.

To study the stability of AT in more detail, its aqueous solution was stored at 100 °C. As shown in Table 4, a significant degradation of the odorant was observable. While about 31% of the AT was degraded after 10 min, a nearly complete decomposition occurred within 60 min (cf. expt 3 and 5; Table 4). These results suggested that especially at higher temperatures a certain amount of AT is always decomposed in parallel with its formation from the precursor HDT.

The activation energy for conversion of HDT into AT was then calculated by using the Arrhenius equation (Barrow, 1972). As shown in Figure 5, the plot log d[concnHDT]/dt vs 1/temp[K] $\times$ 10^{-3} resulted in a straight line, indicating the validity of the Arrhenius equation under the reaction conditions taken into consideration (10 min; temperature range of 50–90 °C). The slope of the straight line (-3.0×10^{-3}) provided the data needed to calculate the activation energy for AT formation from HDT as 57.4 kJ/mol.

In a further set of experiments the influence of the pH on the formation of AT from HDT was studied. The results (Table 5) indicated that increasing the pH from 3.0 to 9.0 at 100 °C significantly increases AT formation (expt 1–5; Table 5). In particular, the yields of AT at pH 9.0 amounted to 15% which was by a factor of nearly 13 higher than the yield at pH 3.0 (cf. expt 1 and 5; Table 5).

Additions of sodium/potassium phosphate ions at pH 7.0 did not influence the formation of AT (cf. expt 4 and 6; Table 5), while heating the precursor HDT in sunflower oil (expt 7; Table 5) increased the amount by 25% in comparison to the reaction in water (expt 4).

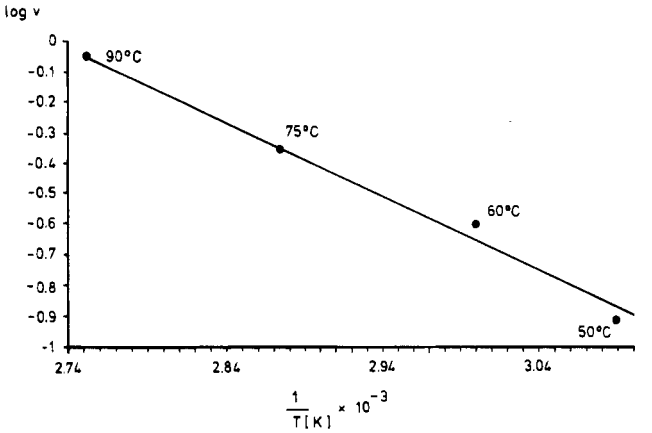

Figure 5. Arrhenius plot (log d[concnHDT]/dt vs 1/temp[K] $\times$ 10^{-3}) calculated for the thermal generation of 2-acetyl-2-thiazoline from 2-(1-hydroxyethyl)-4,5-dihydrothiazole.

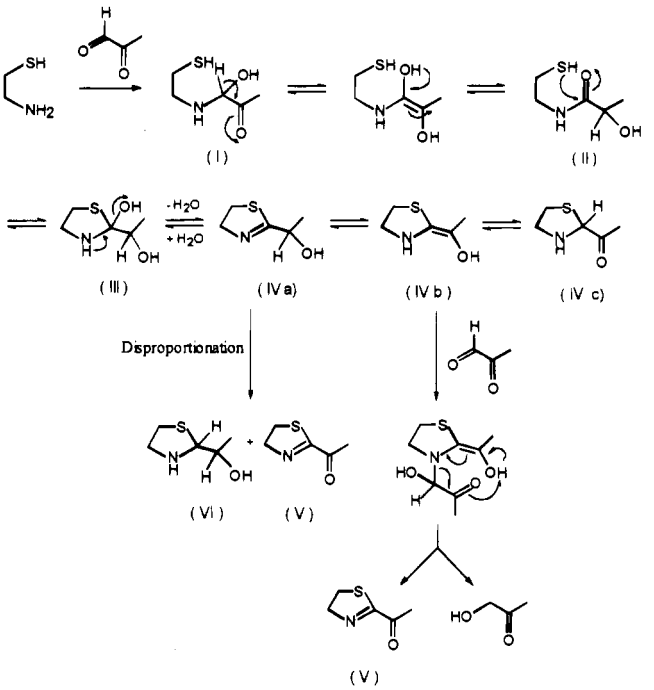

Figure 6. Reaction pathway leading from cysteamine and 2-oxopropanal to 2-acetyl-2-thiazoline via 2-(1-hydroxyethyl)-4,5-dihydrothiazole (HDT) as the key intermediate.

DISCUSSION

The results indicate HDT is a key intermediate in the thermal generation of AT. In Figure 6, a pathway leading to the formation of AT from cysteamine and 2-oxopropanal via HDT is proposed. It can be assumed that the first step is the formation of the aminoacetal **I**. Isomerization of **I** into intermediate **II** enables a nucleophilic attack of the thiol group with formation of the thioacetal **III**. Elimination of water would then yield the 2-(1-hydroxyethyl)-4,5-dihydrothiazole (IVa in Figure 6). A second molecule of 2-oxopropanal then oxidizes the tautomeric amino enol (**IVb**), giving rise to 2-acetyl-2-thiazoline (**V**).

The further experiments have shown that thermal treatment of HDT (**IVa**, Figure 6) either in aqueous solution or in the gas phase (injector of the gas chro-

matograph) generates significant amounts of AT also in the absence of oxidative agents. This result might be explained by a disproportionation reaction of the HDT tautomers **IVb** and **IVc** (Figure 6) generating AT (**V**) and, in addition, 2-(1-hydroxyethyl)thiazolidine (**VI** in Figure 6). However, the latter compound has not yet been identified.

CONCLUSIONS

Thermal degradation of HDT, which easily forms upon storage of aqueous solutions of cysteamine and 2-oxopropanal at low temperatures, has been shown to generate significant amounts of the intensely roasty smelling food flavor compound AT. Cysteamine is proposed to be generated during food processing by an oxidative decarboxylation (Strecker reaction) of the amino acid cysteine, while 2-oxopropanal is assumed to be formed by a thermal cleavage of carbohydrates. As a consequence, the results allow the conclusion that HDT might also be an important intermediate in the generation of AT in foods, such as meat products or roasted sesame seeds. Although AT itself has been shown to be unstable during heat treatment in the presence of water, a significant stabilization was observed in an oil. It may, therefore, be assumed that fat-containing food matrices would favor the stability of AT also in food flavors.

LITERATURE CITED

Barrow, G. M. *Physical Chemistry*, part III; Bohmann and Viehweg: Braunschweig, 1972; pp 295 ff.

Cerny, C.; Grosch, W. Evaluation of potent odorants in roasted beef by aroma extract dilution analysis. *J. Agric. Food Chem.* **1992**, *40*, 322–325.

Cerny, C.; Grosch, W. Quantification of character impact odor compounds of roasted beef. *Z. Lebensm. Unters. Forsch.* **1993**, *196*, 417–422.

Gasser, U.; Grosch, W. Primary odorants of chicken broth. A comparative study with meat broths from cow and ox. *Z. Lebensm. Unters. Forsch.* **1990**, *190*, 1–6.

Guth, H.; Grosch, W. 3-Methylnonane-2,4-dione—an intense odor compound formed during flavor reversion of soya-bean oil. *Fat Sci. Technol.* **1989**, *91*, 225–230.

Guth, H.; Grosch, W. 12-Methyltridecanal, a species-specific odorant of stewed beef. *Lebensm. Wiss. Technol.* **1993**, *26*, 171–177.

Guth, H.; Grosch, W. Identification of the character impact odorants of stewed beef juice by instrumental analyses and sensory studies. *J. Agric. Food Chem.* **1994**, *42*, 2862–2866.

Hartmann, G. J.; Jin, Q. Z.; Collins, G. J.; Lee, K. N.; Ho, C. T.; Chang, S. S. Nitrogen-containing heterocyclic compounds indentified as volatile flavor constituents of roasted beef. *J. Agric. Food Chem.* **1983**, *31*, 1030–1033.

Hayashi, T.; Shibamoto, T. Analysis of methyl glyoxal in foods and beverages. *J. Agric. Food Chem.* **1985**, *33*, 1090–1093.

Hofmann, T.; Schieberle, P. Evaluation of the key odorants in a thermally treated solution of ribose and cysteine by aroma extract dilution analysis. *J. Agric. Food Chem.* **1995**, *43*, 2187–2194.

Hofmann, T.; Hässner, R.; Schieberle, P. Determination of the chemical structure of the intense roasty, popcorn-like odorant 5-acetyl-4,5-dihydro-1,4-thiazine. *J. Agric. Food Chem.* **1995**, *43*, 2195–2198.

Milo, C.; Grosch, W. Changes in the odorants of boiled trouts (*Salmo fario*) as affected by the storage of the raw material. *J. Agric. Food Chem.* **1993**, *41*, 2076–2081.

Sakaguchi, M.; Shibamoto, T. Formation of heterocyclic compounds from the reaction of cysteamine and D-glucose, acetaldehyde, or glyoxal. *J. Agric. Food Chem.* **1978**, *26*, 1179–1183.

Schieberle, P. Primary odorants in popcorn. *J. Agric. Food Chem.* **1991**, *39*, 1141–1144.

Schieberle, P. Studies on the flavor of roasted white sesame seeds. In *Progress in Flavor Precursor Studies*; Schreier, P., Winterhalter, P., Eds.; Allured Publishing: Carol Stream, IL, 1993; pp 343–360.

Silwar, R. HRGC/MS study on the flavor compounds formed in a cysteine/rhamnose model system using roasting conditions. *Z. Lebensm. Unters. Forsch.* **1992**, *195*, 112–119.

Tonsbeek, C. H. T.; Copier, H.; Plancken, A. J. Compounds contributing to beef flavor. Isolation of 2-acetyl-2-thiazoline from beef broth. *J. Agric. Food Chem.* **1971**, *19*, 1014–1016.

Tressl, R.; Helak, B.; Grünewald, K.-G.; Silwar, R. Formation of flavor components from proline, hydroxyproline, and sulfur containing amino acids. In *International Symposium on Food Flavors;* Adda, J., Richard, H., Eds.; Technique et Documentation-Lavoisier: Paris, 1983; pp 207–230.

Received for review June 6, 1995. Accepted August 23, 1995.[⊗]

JF950347Z

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.