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α-Mercaptoketone Formation during the Maillard Reaction of Cysteine and [1-^{13}C]Ribose

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The volatiles formed from [1-^{13}C]-ribose and cysteine during 4 h at 95 °C in aqueous phosphate buffer (pH 5) were analyzed by headspace SPME in combination with GC-MS. The extent and position of the labeling were determined using MS data. The identified volatiles comprised sulfur compounds such as 2-[^{13}C]methyl-3-furanthiol, 2-[$^{13}CH_2$]furfurylthiol, [1-^{13}C]-3-mercaptopentan-2-one, [1-^{13}C]-3-mercaptobutan-2-one, [4-^{13}C]-3-mercaptobutan-2-one, and 3-mercaptobutan-2-one. The results confirm furan-2-carbaldehyde as an intermediate of 2-furfurylthiol, as well as 1,4-dideoxypento-2,3-diulose as an intermediate of 2-methyl-3-furanthiol and 3-mercaptopentan-2-one. Loss of the C-1 and C-5 carbon moieties during the formation of 3-mercaptobutan-2-one suggests two different mechanisms leading to the key intermediate butane-2,3-dione.

KEYWORDS: Maillard reaction; 2-methyl-3-furanthiol; 2-furfurylthiol; 3-mercaptopentan-2-one; 3-mercaptobutan-2-one; [1-^{13}C]ribose; cysteine; 1,4-dideoxypento-2,3-diulose; solid-phase microextraction; Amadori compound; mass spectrometry

INTRODUCTION

Thiols belong to the key aroma compounds of meat flavor. The Maillard reaction between ribose and cysteine is known to be important for the generation of 2-methyl-3-furanthiol, 2-furfurylthiol, 3-mercaptopentan-2-one, 3-mercaptobutan-2-one, and other sulfur odorants in meat as well as in meatlike process flavors (*1*−*6*). Numerous studies have been carried out to gain more insight into the reaction mechanism (*5*, *7*−*13*). Early intermediates such as 1-deoxypento-2,3-diulose and 3-deoxypento-1,2-diulose, as well as secondary intermediates such as 4-hydroxy-5-methyl-(2*H*)-furan-3-one, furan-2-carbaldehyde, butane-2,3-dione, and pentane-2,3-dione, have been proposed to explain their formation (*10*, *14*−*19*).

Recently, Maillard reaction experiments with [$^{13}C_5$]ribose have been performed in our laboratory to further elucidate these formation pathways (*20*). Mixtures of ribose and cysteine, as well as [$^{13}C_5$]ribose, cysteine, and an intermediate [4-hydroxy-5-methyl-(2*H*)-furan-3-one and furan-2-carbaldehyde, respectively] were reacted and the volatiles analyzed by headspace solid-phase microextraction (HS-SPME) in combination with GC-MS. Whereas furan-2-carbaldehyde was confirmed as an important intermediate for 2-furfurylthiol, 4-hydroxy-5-methyl-(2*H*)-furan-3-one was found to play only a minor role in the formation of 2-methyl-3-furanthiol under cooking conditions (95 °C, 4 h). In the formation of 3-mercaptobutan-2-one one carbon unit was lost from ribose, but the rest of the carbon skeleton remained intact. The carbon chain of ribose was also preserved in 3-mercaptopentan-2-one, whereas the isomer 2-mercapto-3-pentanone was not detected. The new key intermediate, 1,4-dideoxypento-2,3-diulose, was proposed for both 2-methyl-3-furanthiol and 3-mercaptopentan-2-one formation.

The goal of this study was to further elucidate the generation of sulfur volatiles from ribose and cysteine, particularly the chemical pathways leading to α-mercaptoketones. [1-^{13}C]Ribose was used in the model reaction with cysteine to find out how the original ribose chain is arranged in 3-mercaptopentan-2-one and which carbon end is split off from the pentose during the formation of 3-mercaptobutan-2-one.

MATERIALS AND METHODS

Chemicals. Chemicals were of analytical grade. D-Ribose and L-cysteine were from Fluka (Buchs, Switzerland) and dipotassium hydrogenphosphate and potassium dihydrogenphosphate from Merck (Darmstadt, Germany). [1-^{13}C]Ribose (99% enrichment) was from Cambridge Isotope Laboratories (Andover, MA).

Reactions. A solution of cysteine (5.84 mg) and ribose (21.75 mg) in potassium phosphate buffer (472 mg; 0.5 mol/L; pH 5.00) was thermally treated in 2 mL glass vials for 4 h at 95 °C in a heated metal block (Reacti-Therm, stirring/heating module, Pierce Chemical Co., Rockford, IL). The molar ratio between cysteine and ribose was 1:3. Another experiment was carried out using [1-^{13}C]ribose instead of ribose.

Analysis. Both samples were analyzed by headspace solid-phase microextraction in combination with gas chromatography coupled to mass spectrometry (HS-SPME-GC-MS). The headspace above the reacted samples in the glass vials was exposed for 60 min at 20 °C to the PDMS-DVB fiber (film thickness = 65 μm, Supelco) without agitation. The loaded SPME fiber was placed for 5 min in the GC injector (0.75 mm i.d. liner, Supelco) heated at 250 °C. Analyses were performed on a GC 6890A equipped with an HP-PONA column (50

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Table 1. MS Spectra of Compounds Formed from Cysteine and [1-^{13}C]Ribose

no.	compound	RI (OV-1)	reaction cysteine + ribose (reference) *m/z* (%)	reaction cysteine + [1-^{13}C]ribose *m/z* (%)	^{13}C-labeling distribution (no/$^{13}C_1$/$^{13}C_2$)
1	furan	500	38 (14), 39 (80), 40 (8), 68 (100), 69 (5)	38 (14), 39 (77), 40 (9), 68 (100), 69 (3)	100/0/0
2	2-methylfuran	586	39 (26), 50 (10), 51 (9), 53 (51), 81 (54), 82 (100)	39 (17), 40 (13), 52 (11), 53 (15), 54 (45), 55 (14), 82 (76), 83 (100)	0/100/0
3	thiazole	709	45 (7), 57 (14), 58 (58), 60 (4), 85 (100), 87 (3)	57 (25), 58 (96), 60 (6), 85 (66), 86 (100), 87 (7), 88 (6)	35/65/0
4	2-methylthiophene	756	39 (5), 45 (9), 97 (100), 98 (56), 99 (8)	39 (3), 40 (3), 45 (8), 54 (4), 97 (4), 98 (100), 99 (60), 100 (5)	0/100/0
5	3-mercaptobutan-2-one	782	43 (100), 58 (46), 60 (29), 61 (82), 104 (48)	43 (100), 44 (26), 58 (69), 60 (36), 61 (70), 62 (30), 104 (33), 105 (34)	54/46/0
6	furan-2-carbaldehyde	801	29 (8), 39 (34), 67 (6), 95 (94), 96 (100)	30 (5), 38 (11), 39 (33), 67 (11), 96 (98), 97 (100)	0/100/0
7	2-methyl-3-furanthiol	850	43 (13), 71 (18), 85 (25), 113 (24), 114 (100)	44 (15), 71 (16), 86 (25), 114 (25), 115 (100)	0/100/0
8	3-mercaptopentan-2-one	871	39 (13), 41 (60), 43 (100), 47 (40), 74 (59), 75 (71), 118 (25)	39 (13), 41 (59), 44 (100), 47 (41), 74 (58), 75 (68), 119 (25)	0/100/0
9	2-furfurylthiol	883	53 (39), 81 (100), 114 (35)	54 (36), 82 (100), 115 (33)	0/100/0
10	2-methyl-3-(methylthio)furan	933	51 (17), 99 (15), 113 (60), 128 (100)	114 (81), 129 (100), 130 (17)	0/87/13
11	3-thiophenethiol	940	45 (15), 58 (6), 71 (55), 116 (100)	45 (15), 58 (7), 71 (54), 116 (100)	100/0/0
12	2-methyl-3-thiophenethiol	1042	45 (19), 59 (14), 69 (13), 85 (9), 97 (48), 129 (45), 130 (100)	45 (16), 60 (14), 69 (7), 70 (9), 85 (9), 86 (8), 97 (16), 98 (59), 130 (64), 131 (100)	0/100/0

m × 0.20 mm × 0.50 μm) coupled to an MSD 5973 (Agilent, Palo Alto, CA). After the SPME device had been inserted into the injector, the oven program was started and the temperature raised at 6 °C/min from 35 to 240 °C and held for 10 min isothermally. Mass spectra in the electron impact mode (EI) were generated at 70 eV and at a scan range from *m/z* 28 to 350.

RESULTS AND DISCUSSION

Cysteine and [1-^{13}C]ribose (molar ratio 1:3) were reacted at 95 °C for 4 h in an aqueous buffer (pH 5). A similar experiment was conducted with unlabeled ribose instead of [1-^{13}C]ribose, and both reaction products were analyzed by headspace SPME coupled to GC-MS. **Table 1** lists the compounds identified along with the mass spectra data obtained from both trials. Comparison of the MS data gave labeling extent as well as the position of the ^{13}C atom in the molecules generated from labeled ribose and cysteine. The proposed structures are depicted in **Figure 1**.

The mass spectra of 3-mercaptopentan-2-one revealed that exclusively a singly labeled compound (**8**) was formed from [1-^{13}C]ribose. Earlier results had shown that no fragmentation of the ribose C-skeleton occurred during the reaction (*20*). The base peak at *m/z* 44 corresponds to $(^{13}CH_3CO)^+$ and the signal at *m/z* 75 to the loss of the corresponding neutral fragment ($^{13}CH_3CO$) from the molecular ion at *m/z* 119. These findings suggest [1-^{13}C]-**8** as molecular structure with the labeling position at C-1, which is in agreement with the formation pathway proposed earlier from ribose via 1,4-dideoxypento-2,3-diulose as intermediate. This pathway is also concordant with the absence of the isomer 2-mercapto-3-pentanone (*20*).

The MS data of 3-mercaptobutan-2-one (**5**) formed in the reaction between cysteine and [1-^{13}C]ribose reveal a mixed spectrum of unlabeled and ^{13}C-labeled **5**. Integration of the molecular ion signals at *m/z* 104 and 105 indicates 54% unlabeled (**5a**) and 46% monolabeled 3-mercaptobutan-2-one. The fragments *m/z* 43 and 44 correspond to the loss of $(^{12}CH_3CO)^+$ and $(^{13}CH_3CO)^+$ ions, respectively, from the molecular ion. The ratio of the corresponding integrated peaks in the ion chromatograms was found to be 74:26 (*m/z* 43:44). Hence, 26% of **5** is labeled at the C-1 atom (**5b**), and consequently the remaining 20% of labeled compound consists of [4-^{13}C]-**5** (**5c**), because the C_4 chain is not fragmented under the reaction conditions (*20*). These interesting results suggest that two simultaneous pathways exist for the generation of butane-2,3-dione, which is proposed as an intermediate in the literature (*16*, *17*). Unlabeled or 1-^{13}C-labeled butane-2,3-dione forms

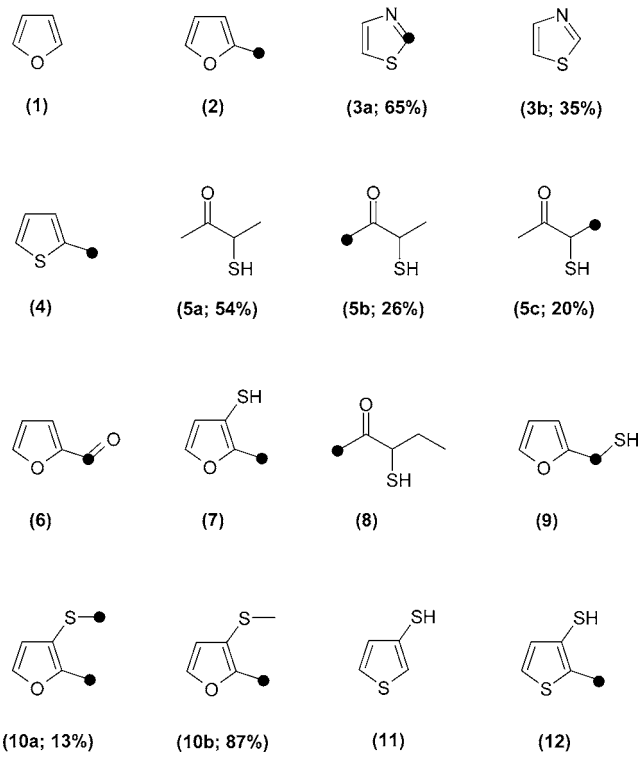

Figure 1. Compounds formed from [1-^{13}C]ribose and cysteine. ^{13}C-Labeling position is marked with (●).

depending on whether ribose loses its C-1 or C-5 moiety. Recently, Schieberle and co-workers showed that at a higher reaction temperature (180 °C) and low water content (10%) butane-2,3-dione is not formed from an intact carbohydrate chain, but mainly from C_3/C_1 recombination (*21*). Under cooking conditions (95 °C, 4 h), as used in the present study, fragmentation was negligible. Further reaction with hydrogen sulfide stemming from cysteine yields **5a** from the unlabeled butane-2,3-dione and a mix of both isomers **5b** and **5c** from the labeled intermediate, respectively.

Figure 2 illustrates the proposed formation pathway to unlabeled butane-2,3-dione and **5a** from [1-^{13}C]ribose and cysteine. Rearrangement of the Schiff base gives the Amadori compound **13**, which, after a further rearrangement of the carbonyl group and loss of water, is transformed into *N*-([1-^{13}C]-2-hydroxy-3,4-dioxopentyl)cysteine (**14**). Recently, de Roos has confirmed the role of Amadori compounds of cysteine with

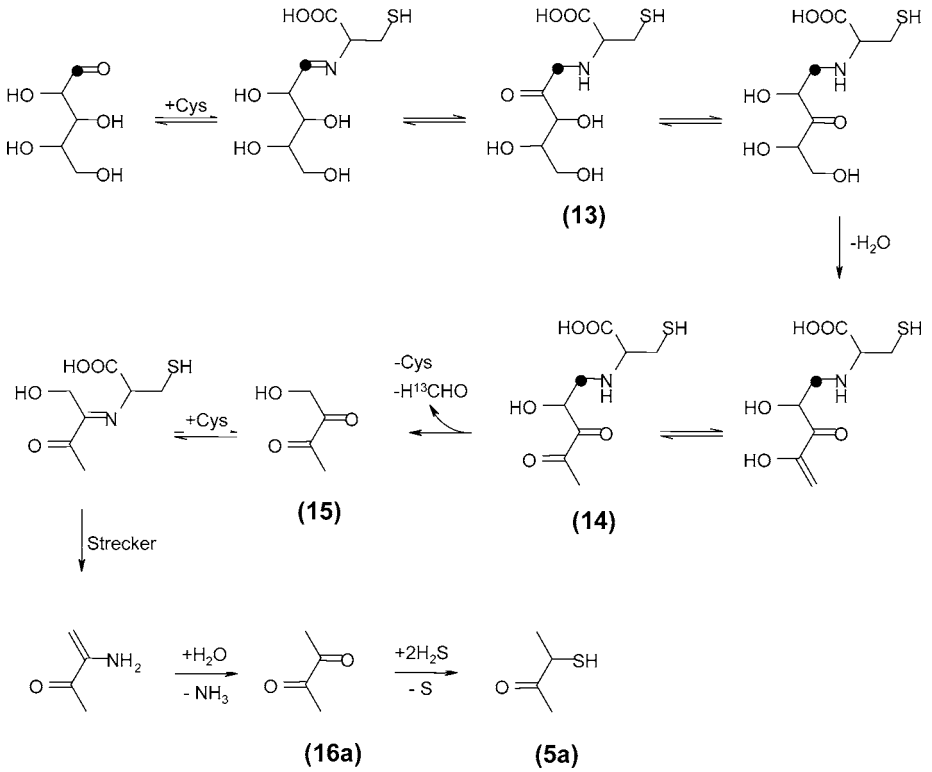

Figure 2. Proposed formation pathway for unlabeled 3-mercaptobutan-2-one from [1-^{13}C]ribose and cysteine via the 1,5-dideoxyosone pathway (● = ^{13}C).

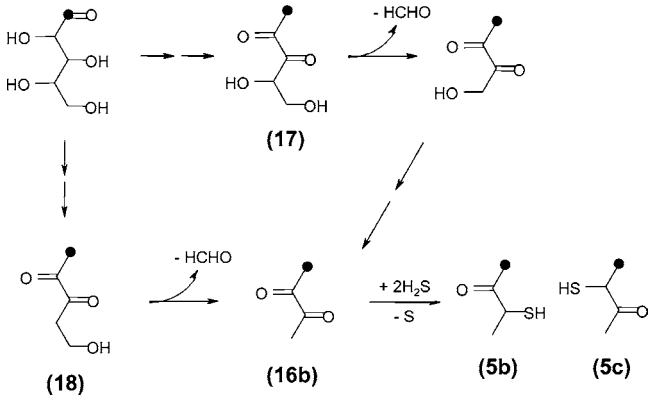

Figure 3. Proposed formation pathway for ^{13}C-labeled 3-mercaptobutan-2-one from [1-^{13}C]ribose and cysteine. ^{13}C-Labeling position is marked with (●).

sugars for meat flavor generation (*22*). N^6-(2-Hydroxy-3,4-dioxo-pentyl)lysine, a 5-deoxyosone similar to **14**, has been identified in the reaction of arabinose with lysine (*23*). In a retro-Mannich reaction **14** eliminates cysteine and [1-^{13}C]formaldehyde to form 1-hydroxybutane-2,3-dione (**15**). Strecker degradation of **15** and loss of ammonia result in unlabeled butane-2,3-dione (**16a**) and finally **5a**.

Figure 3 explains the formation of [1-^{13}C]-butane-2,3-dione (**16b**) from [1-^{13}C]ribose and the consecutive reaction to labeled **5**. One possible route is the retroaldol reaction of the postulated intermediate [1-^{13}C]-1,4-dideoxypento-2,3-diulose (**18**) with loss of formaldehyde at the C-5 atom leading to **16b**. Another possible way includes the primary Maillard product [1-^{13}C]-1-deoxypentosone (**17**), which undergoes retroaldolization to [4-^{13}C]-1-hydroxybutane-2,3-dione. Strecker degradation, as detailed in **Figure 2**, leads to **16b**. Finally, the reaction of the diketone with hydrogen sulfide generates both labeled 3-mercaptobutan-2-one isomers **5b** and **5c**.

Two compounds, furan (**1**) and 3-thiophenethiol (**11**), were found exclusively unlabeled. Furan (**1**) was formed through loss of the ^{13}C atom from [1-^{13}C]ribose during the reaction, whereas 3-thiophenethiol (**11**) stems from cysteine (*18*, *20*, *24*). Sixty-five percent of thiazole (**3**) from [1-^{13}C]ribose and cysteine was found labeled. The labeling position was assigned to the C-2 atom according to the loss of hydrogen [^{13}C]cyanide as indicated by the signal at *m*/*z* 58 in the mass spectrum (*25*). The formation of **3a** and **3b** can be explained by the condensation of cysteamine with [^{13}C]formaldehyde and unlabeled formaldehyde, respectively (*26*), followed by oxidation of the resulting thiazolidine. [^{13}C]Formaldehyde originates from the C-1 atom of [1-^{13}C]ribose. The mass spectra of 2-methylfuran (**2**) and 2-methyl-3-furanthiol (**7**) are characterized by the loss of *m*/*z* 29 ($H^{12}CO$) from the molecular ion and those of 2-methylthiophene (**4**) and 2-methyl-3-thiophenethiol (**12**) by the occurrence of the fragment *m*/*z* 45 $(H^{12}CS)^+$. These unlabeled fragments stem from the C-5 atom of furan or the thiophene ring and indicate that the four molecules are not ^{13}C-labeled at this position when [1-^{13}C]ribose is used as reactant. Previous results did not indicate a substantial fragmentation of the C-skeleton (*20*) during the reaction, and consequently a ^{13}C-labeled methyl group is proposed for **2**, **4**, **7**, and **12**. Formation of **7** from the fragments hydroxyacetaldehyde and 1-mercapto-2-propanone, as proposed in ref *27*, was not relevant under the reaction conditions used in this study.

The spectrum of the singly ^{13}C-labeled furfurylthiol (**9**) shows fragments of *m*/*z* 115, 82, and 54, which indicate the loss of SH (*m*/*z* 33) from the molecular ion and a further loss of ^{12}CO (*m*/*z* 28) from the base peak ion *m*/*z* 82 corresponding to an unlabeled carbon at C-5. Therefore, the labeled carbon atom of [1-^{13}C]ribose is assigned to the methylene group of **9**, this finding being in accordance with the formation from ribose via 3-deoxypento-1,2-diulose and furfural (*20*, *28*).

For 2-methyl-(3-methylthio)furan (**10**), only singly labeled (**10b**) and doubly labeled compound (**10a**) were found. A ratio

between the integrated molecular ion signal of **10b** (*m*/*z* 129) and that of **10a** (*m*/*z* 130) was 87:13. A previous study showed that the methylthio carbon stems partly from ribose and partly from cysteine (*20*). The results obtained with [1-^{13}C]ribose indicate that only part of the methylthio carbon stemming from ribose originates from the C-1 carbon atom.

The investigations could elucidate the different pathways that lead to α-mercaptoketones from ribose and cysteine during heating in aqueous phosphate buffer (pH 5). The intact ribose skeleton is incorporated into 3-mercaptopentan-2-one (**8**) with the C-1 ribose carbon atom forming the C-1 moiety of **8**. This finding is in agreement with the earlier proposed pathway via 1,4-dideoxypento-2,3-diulose as intermediate (*20*). Two equally important mechanisms play a role in the formation of 3-mercaptobutan-2-one, with loss of the C-1 and C-5 ribose carbon atoms, respectively. The results from the labeling experiments corroborate the diketone butane-2,3-dione as key intermediate.

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