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Nonvolatile Oxidation Products of Glucose in Maillard Model Systems: Formation of Saccharinic and Aldonic Acids and Their Corresponding Lactones

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By using pyrolysis−gas chromatography−mass spectrometry-based methodologies, nonvolatile oxidation products of isotopically labeled glucose/glycine model systems were studied through a postpyrolytic in situ derivatization technique by using trimethylsilyldiethylamine. Analysis of the data indicated that the known reactive sugar intermediates such as glucosone and its deoxy derivatives can undergo in Maillard model systems three types of transformations: oxidation of the aldehydic groups into carboxylic acids, oxidative cleavage of α-dicarbonyl moieties into aldonic acids, and benzylic acid rearrangement of 1-deoxy-glucosone into saccharinic acids. The aldonic and saccharinic acids were identified through silylation of their lactone derivatives, and their origin was verified through ^{13}C-labeling studies. The following lactones were identified in glucose and glucose/glycine model systems: *trans*-dihydro-3,4-bis[(trimethylsilyl)oxy]-2(3*H*)-furanone, *cis*-dihydro-3,4-bis[(trimethylsilyl) oxy]-2(3*H*)-furanone, 2-C-methyl-2,3,5-tris-O-(trimethylsilyl)-D-ribonic acid γ-lactone, 3-deoxy-2,5,6-tris-*O*-(trimethylsilyl)-D-ribo-hexonic acid γ-lactone, 2-deoxy-3,5-bis-*O*-(trimethylsilyl)-pentonic acid γ-lactone, and 2,3,5-tris-*O*-(trimethylsilyl)-D-arabinonic acid γ-lactone. The observed reduction in color and aroma in Maillard reactions performed under oxidative conditions may be attributed to the oxidation of reactive dicarbonyls into the corresponding carboxylic acids or their corresponding lactones.

KEYWORDS: Oxidative pyrolysis; postpyrolytic derivatization technique; oxidation of glucose; lactones; aldonic acids; saccharinic acid; ^{13}C-labeled glucose; pyrolysis−gas chromatography−mass spectrometry (Py-GC/MS)

INTRODUCTION

The main feature of the degradative reactions of carbohydrates occurring during Maillard reactions is the formation of sugar-derived building blocks of Maillard products. The cleavage of the intact sugar-derived intermediates such as glucosone, 1-deoxy-glucosone, and 3-deoxyglucosone leads to the formation of smaller and more reactive α-dicarbonyl compounds as carbon skeletons for various precursors essential for the formation of different heterocyclic aroma compounds (*1*). Carbohydrate degradations during Maillard reactions play a crucial role in determining the product distribution of various sugar-derived Maillard products, especially in model systems containing amino acids with alkyl side chains (*2, 3*). Weenen and Apeldoorn (*4*) investigated carbohydrate degradations in different L-alanine model systems and quantified various dicarbonyl compounds through reaction with o-diaminobenzene. They attributed the origin of these compounds mainly to the fragmentation of glucosone and deoxyglucosone formed through oxidative transformations and reactions with amino acids. Glucosone and deoxy-glucosone are α-dicarbonyl intermediates that can undergo α-dicarbonyl cleavage reactions to produce different carboxylic and aldonic acids. Recent publications (*5, 6*) have identified two distinct pathways for the formation of such acids. A major pathway involves isomerization of the reactive α-dicarbonyl moiety into the β-dicarbonyl form, followed by hydrolytic cleavage generating carboxylic acids. For example, 1-deoxy-glucosone can undergo such cleavage and produce acetic acid plus a keto sugar. Alternatively, α-dicarbonyl intermediates can directly undergo an oxidative α-dicarbonyl cleavage. In this proposed mechanism, molecular oxygen is incorporated at any one of the carbonyl carbons of the dicarbonyl moiety. This step is followed by a single-electron transfer, a Baeyer–Villiger-type rearrangement, and finally hydrolysis to produce two carboxylic acid fragments (**Figure 1**). Nonvolatile acids and their corresponding lactones from glucose and glycine models have been identified by utilizing thin-layer chromatography, high-pressure liquid chromatography (*7*), and derivatization with benzoimidazole (*8*). It was assumed that they had

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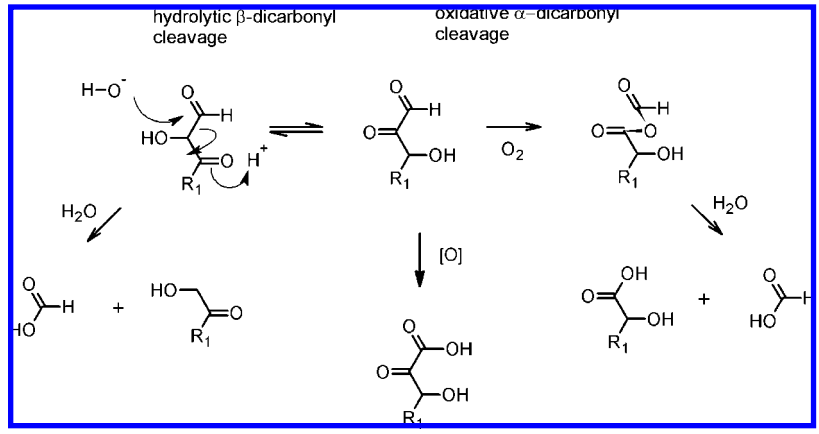

Figure 1. Oxidation pathways of reactive α-dicarbonyl intermediates of glucose (based on refs *5* and *6*).

Table 1. Mass Spectrometric Data and Retention Times of Silylated Lactones

cis-Dihydro-3,4-bis[(trimethylsilyl)oxy]-2(3H)-furanone **(1a)** (22.59 min)	
NIST library	147 (100), 73 (88), 45 (28), 247 (27), 75 (23), 101 (20), 59 (16), 116 (14), 148 (14), 103 (13), 129 (9), 262 (6)
experimental results	147 (100), 73 (45), 45 (15), 247 (42),75 (23), 101 (15), 59 (8), 116 (10), 148 (18), 103 (6), 129 (5), 262 (11)
trans-Dihydro-3,4-bis[(trimethylsilyl)oxy]-2(3H)-furanone **(1b)** (23.45 min)	
NIST library	147 (100), 73 (88), 45 (28), 247 (27), 189 (5), 75 (23), 101 (19), 59 (16), 116 (14), 148 (14), 103 (13), 129 (9), 262 (6)
experimental results	147 (100), 73 (77), 45 (24), 247 (58), 189 (28), 75 (10), 101 (18), 59 (10), 116 (9), 148 (19), 103 (20), 129 (8), 262 (8)
2-C-Methyl-2,3,5-tris-O-(trimethylsilyl)-D-ribonic Acid γ-Lactone **(2)** (26.66 min)	
NIST library	73 (100), 217 (54), 147 (41), 117 (36), 378 (26), 218 (23), 87 (18), 75 (17), 74 (9), 231 (9), 260 (7)
experimental results	73 (100), 217 (90), 147 (60), 117 (24), 378 (38), 218 (50), 87 (0), 75 (15), 74 (10), 231 (10), 260 (37)
3-Deoxy-2,5,6-tris-O-(trimethylsilyl)-D-ribo-hexonic Acid Lactone **(3)** (28.46 min)	
NIST library	73 (100), 129 (31), 75 (22), 273 (19), 103 (19), 246 (18), 147 (18), 205 (15),155 (15), 74 (14), 245 (10), 378 (8)
experimental results	73 (100), 129 (47), 75 (13), 273 (42), 103 (13), 246 (35), 147 (65), 205 (10), 155 (70), 74 (10), 245 (4), 378 (38)
2-Deoxy-3,5-bis-O-(trimethylsilyl)-pentonic Acid γ-Lactone **(4)** (24.84 min)	
NIST library	73 (100), 75 (89), 103 (30), 45 (29), 97 (22), 47 (19), 28 (16), 147 (12), 59 (12), 101 (11), 261 (1)
experimental results	73 (100), 75 (19), 103 (40), 45 (25), 97 (58), 47 (6), 28 (0), 147 (53), 59 (14), 101 (27), 261 (1)
2,3,5-Tris-O-(trimethylsilyl)-D-arabinonic Acid γ-Lactone **(5)** (26.57 min)	
NIST library	73 (100), 117 (24), 147 (16), 189 (12), 217 (12), 231 (12), 75 (10), 45 (9), 74 (9), 204 (8), 364 (7)
experimental results	73 (100), 117 (19), 147 (35), 189 (15), 217 (21), 231 (38), 75 (13), 45 (22), 74 (12), 204 (33), 364 (29)

been formed via benzylic acid rearrangement or fragmentation. Several nonvolatile lactones and acids were also identified via methylation and silylation by Petersson (*9*). Here, we report the first systematic study on oxidative transformations of α-dicarbonyl intermediates originating from glucose in a Maillard model system by using oxidative pyrolysis and ^{13}C-labeled precursors to provide further evidence for the structure and origin of the resulting saccharinic and aldonic acids or their lactone derivatives.

MATERIALS AND METHODS

All reagents and chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI). The labeled sugars [1-^{13}C]glucose (99%), [2-^{13}C]glucose (99%), [3-^{13}C]glucose (99%), [4-^{13}C]glucose (99%), [5-^{13}C]glucose (99%), [6-^{13}C]glucose (99%), [U6-^{13}C]glucose (99%), [1-^{13}C]glycine (99%), [2-^{13}C]glycine (99%), and [^{15}N]glycine (98%) were purchased from Cambridge Isotope Laboratories (Andover, MA).

Pyrolysis−Gas Chromatography−Mass Spectrometry (Py-GC/MS) Analysis. A Varian CP-3800 gas chromatograph coupled to a Saturn 2000 ion trap detector interfaced to a CDS Pyroprobe 2000 unit through a valved interface (CDS 1500) was used for Py-GC/MS analysis. In all experiments, the glucose/glycine model mixtures (0.5 mg, equimolar) were introduced inside the quartz tube (0.3 mm thickness), which was plugged with quartz wool, and inserted into the coil probe. Prior to pyrolysis, argon gas was directed at the entrance of the pyroprobe interface to prevent the introduction of air into the pyroprobe interface. The temperature of the pyroprobe interface was set at 250 °C. Model systems were initially pyrolyzed at 250 °C with a total heating time of 20 s, three consecutive times. Samples were left in the interface for a total of 2 min, then removed, and immediately cooled with argon gas to prevent oxidative browning. After cooling, 1 μL of derivatization agent trimethylsilyldiethylamine (TMSDEA) was injected onto the nonvolatile residue inside the quartz tube. After 5 min, the sample was introduced into the interface under a steady stream of argon. The sample was repyrolyzed at 100 °C, ramped at 10 °C /s up to 175 °C for 20 s, and left in the interface for a total of 2 min. The

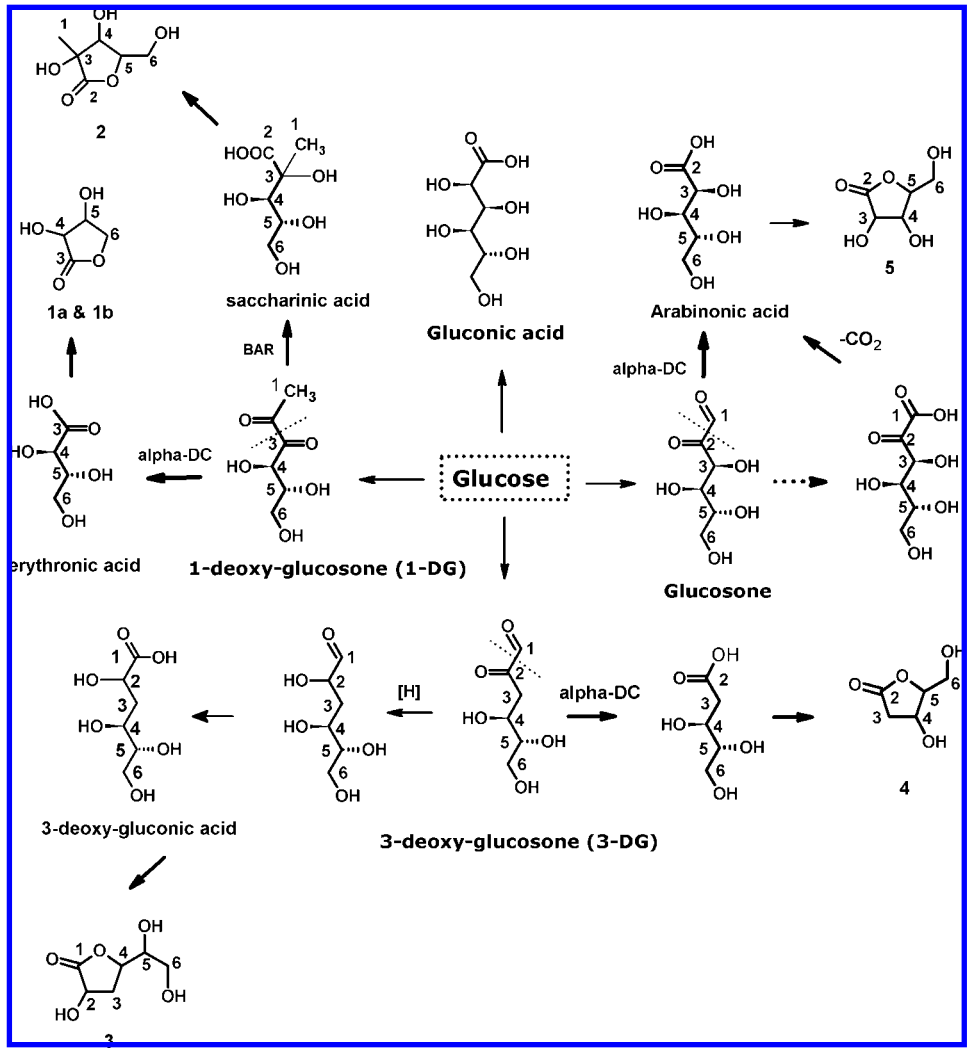

Figure 2. Proposed α-dicarbonyl precursors of various lactones identified in glucose/glycine model system. The numbers indicate the positions of the glucose carbon atoms. alpha-DC, oxidative α-dicarbonyl cleavage; BAR, benzylic acid rearrangement.

Table 2. Percent Label[a] Distribution in Silylated Derivatives Identified in D-Glucose-U-$^{13}C_6$/Glycine Model System Shown in **Table** 1 and **Figure** 2

	compound					
	1a	**1b**	**2**	**3**	**4**	**5**
M + 4	100	100	0	0	0	0
M + 5	0	0	0	0	100	100
M + 6	0	0	100	100	0	0

[a] A similar label incorporation pattern was also observed in the absence of glycine.

initial temperature of the column was set at −5 °C for 12 min and then increased to 50 °C at a rate of 50 °C/min; immediately, the temperature was further increased to 250 °C at a rate of 8 °C/min and kept at 250 °C for 5 min. A constant flow of 1.5 mL/min was used during analysis. The capillary direct MS interface temperature was 250 °C; the ion source temperature was 180 °C. The ionization voltage was 70 eV, and the electron multiplier was set at 2047 V. The mass range analyzed was 29–300 amu. The column was a fused silica DB-5 MS column (50 m length, 0.2 mm i.d., and 0.33 μm film thickness; J&W Scientific). The identity and purity of the chromatographic peaks were determined by using NIST AMDIS version 2.1 software. The reported percent label incorporation values (corrected for natural abundance and for percent enrichment) are the average of duplicate analyses and are rounded off to the nearest multiple of 5%.

Oxidative Py-GC/MS. Pyrolysis under air or in the presence of water was achieved through modification of the above-mentioned GC to allow gas stream switching and subsequent isolation of the pyrolysis

Table 3. Percent Label[a] Incorporation (M + 1 Peak) in Silylated Derivatives Identified in Glucose/Glycine Model System[b] Shown in **Table** 1 and **Figure** 2

	compound					
	1a	**1b**	**2**	**3**	**4**	**5**
D-glucose-6-^{13}C/glycine	100	100	100	100	100	100
D-glucose-5-^{13}C/glycine	100	100	100	100	100	100
D-glucose-4-^{13}C/glycine	100	100	100	100	100	100
D-glucose-3-^{13}C/glycine	100	100	100	100	100	100
D-glucose-2-^{13}C/glycine	0	0	100	100	100	100
D-glucose-1-^{13}C/glycine	0	0	100	100	0	0
D-glucose/glycine-1-^{13}C	0	0	0	0	0	0
D-glucose/glycine-2-^{13}C	0	0	0	0	0	0
D-glucose/glycine-^{15}N	0	0	0	0	0	0

[a] All singly labeled. [b] A similar label incorporation pattern was also observed in the absence of glycine.

chamber from the analytical stream. The pyrolysates generated under air or in the presence of moisture were initially collected onto the trap, which retained the organic volatiles and vented the carrier gas (air) and/or moisture. The trap was subsequently flushed with helium and heated to desorb the collected volatiles (*10*).

RESULTS AND DISCUSSION

Py-GC/MS-based methodologies were developed to analyze nonvolatile residues of Maillard-reaction products generated

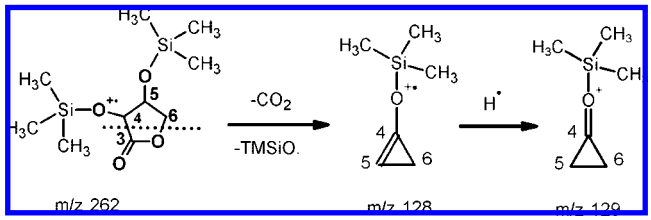

Figure 3. Proposed fragmentation of the parent ion at *m/z* 262 of dihydro-3,4-bis[(trimethylsilyl)oxy]-2(3H)-furanone (**1**) to form an ion at *m/z* 129. The numbers indicate the positions of the glucose carbon atoms.

Table 4. Percent ^{13}C-Label[a] Distribution in Ion at *m/z* 129 of Dihydro-3,4-bis[(trimethylsilyl)oxy]-2(3H)-furanone

	compound			
	M	M + 1	M + 2	M + 3
D-glucose-U-$^{13}C_6$/glycine	0	0	0	100
D-glucose/glycine	100	0	0	0
D-glucose-6-^{13}C/glycine	0	100	0	0
D-glucose-5-^{13}C/glycine	0	100	0	0
D-glucose-4-^{13}C/glycine	0	100	0	0
D-glucose-3-^{13}C/glycine	100	0	0	0
D-glucose-2-^{13}C/glycine	100	0	0	0
D-glucose-1-^{13}C/glycine	100	0	0	0
D-glucose/glycine-1-^{13}C	100	0	0	0
D-glucose/glycine-2-^{13}C	100	0	0	0
D-glucose/glycine-^{15}N	100	0	0	0

[a] A similar label incorporation pattern was also observed in the absence of glycine.

through pyrolysis under air or helium atmosphere. The analysis of the nonvolatile coumponds was achieved through a postpyrolytic in situ derivatization technique using trimethylsilyldiethylamine (TMSDEA), and pyrolysis under air was achieved through modification of the GC equipped with a sample concentration trap to allow gas stream switching and subsequent isolation of the pyrolysis chamber from the analytical stream (for details, see ref *10*). This technique was recently applied to study hydroxylated benzene derivatives formed in Maillard model systems (*11*).

In order to distinguish the oxidation products in glucose/glycine model systems, pyrolysis was conducted under both air and helium atmospheres. Chromatographic peaks that showed relative enhancements (at least 2-fold) in intensity under oxidative pyrolysis were targeted for further analysis. Most of the peaks in this category that could be identified through NIST library searches were determined to be lactones (**Table 1**) derived through intramolecular esterification of aldonic and saccharinic acids. They represent almost 40% of the total peak area of the derivatized nonvolatile compounds generated under these experimental conditions. Many of the derivatized lactones generated from glucose/glycine model systems were also identified when glucose or gluconic acid was used. Although it is plausible that amino acids can be indirectly involved in the formation of lactones via Amadori and deoxyosone generation, some lactones were found to be formed more efficiently from glucose oxidation alone, perhaps because of the further interaction of the reactive 1- and 3-deoxyosones with the added glycine. In fact, only 2,3,5-tris-O-(trimethylsilyl)-D-arabinonic acid-γ-lactone (see **Figure 2**) was produced in higher amounts in the presence of glycine. Labeling studies have allowed us to propose the primary glucose oxidation products, such as glucosone and 1- and 3-deoxyosones, as precursors of aldonic and saccharinic acid lactones as shown in **Figure 2** and listed in **Table 1**.

Oxidation of 1-Deoxy-glucosone. The *cis*- and *trans*-dihydro-3,4-bis[(trimethylsilyl)oxy]-2(3H)-furanones (silylated structure **1** in **Figure 2**) were the smallest lactones identified. Inspection of **Table 2** (values generated with glucose-U-$^{13}C_6$) shows that lactones **1a** and **1b** incorporate only four carbon atoms from glucose, and labeling studies shown in **Table 3** suggest that the lactone ring consists of glucose carbon atoms of C-3 to C-6 formed through the loss of C-1 and C-2 atoms. Their formation is proposed to proceed via 1-deoxy-glucosone that can undergo oxidative α-dicarbonyl cleavage and produce erythronic acid (*6*). The resulting acid, having lost C-1 and C-2 atoms, can lactonize, forming structures **1a** and **1b**. Enolization of 1-deoxy-glucosone can explain the formation of isomeric products. Further confirmation of the proposed structure was provided by investigating the label incorporation in the mass spectral fragment at *m/z* 129, detected in the mass spectrum of **1**. This ion can be generated through decarboxylation and loss of TMS moiety from **1** as shown in **Figure 3**. If the lactonization was initiated through erythronic acid as proposed in **Figure 2**, the resulting *m/z* 129 should only contain the carbon atoms C-4, C-5, and C-6. Inspection of **Table 4** confirms the above prediction.

In addition to the oxidative α-dicarbonyl cleavage shown above, 1-deoxy-glucosone can also undergo the well-known benzylic acid rearrangement (see **Figure 4**) to form saccharinic acids that are able to lactonize and generate ribonic acid 2-C-methyl-γ-lactone (**2** in **Figure 2**), detected as 2-*C*-methyl-2,3,5-tris-O-(trimethylsilyl)-ribonic acid γ-lactone. Inspection of **Tables 2** and **3** indicates that this lactone, as expected, incorporates all the carbon atoms of glucose. Partial structural evidence for lactone **2** was obtained through the analysis of the mass spectral fragmentation patterns of labeled analogues, such as identification of the fragment at *m/z* 217 (**Figure 5**). The label incorporation pattern (**Table 5**) of the ion at *m/z* 217 is consistent with the proposed structure assigned to the parent ion at *m/z* 378. Recently, this lactone was synthesized (*12*) in 16% yield, by treating Amadori product of dibenzylamine with calcium hydroxide.

Oxidation of 3-Deoxy-glucosone/Gluconic Acid. Although **3** can be formed through reduction and oxidation steps from 3-deoxy-glucosone followed by lactonization as shown in **Figure 2**, it could also be envisaged to form this compound from the dehydration of gluconic acid followed by reduction/lactonization steps. Irrespective of the exact origin, both are reasonable precursors known to form in Maillard model systems. The complete incorporation of all the six glucose carbon atoms was confirmed by using labeling experiments as shown in **Tables 2** and **3**. In addition, **Figure 6** shows the fragmentation of the parent ion at *m/z* 378 and the formation of ions at *m/z* 245 and 155. As observed for the other lactones, *m/z* 378 loses a carbon dioxide molecule. This step is followed by a loss of TMS moiety to generate *m/z* 245 and the subsequent loss of another TMS moiety to form the ion at *m/z* 155. The label incorporation patterns in these two fragments shown in **Table 6** are consistent with the structure of the proposed precursor. In addition, 3-deoxy-glucosone can also undergo oxidative α-dicarbonyl cleavage (*6*) similar to 1-deoxy-glucosone and produce 2-deoxy-pentonic acid that is able to lactonize into structure **4**, as shown in **Figure 2**. The confirmation of the loss of the C-1 carbon atom from glucose in structure **4** can be seen in **Tables 2** and **3**.

Oxidation of Glucosone. Only one product (**5** in **Figure 2**) could be traced back to glucosone as a precursor. Glucosone, similar to 1- and 3-deoxy-glucosone, can undergo oxidative α-dicarbonyl cleavage (*6*) to form ribonic and/or arabinonic acid through the enolization of the C-2−C-3 bond of the glucosone.

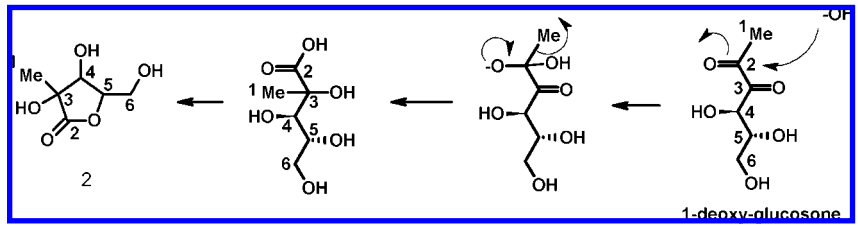

Figure 4. Benzylic acid rearrangement of 1-deoxy-glucosone to form 2-*C*-methyl-D-ribonic acid γ-lactone (**2**). The numbers indicate the positions of the glucose carbon atoms.

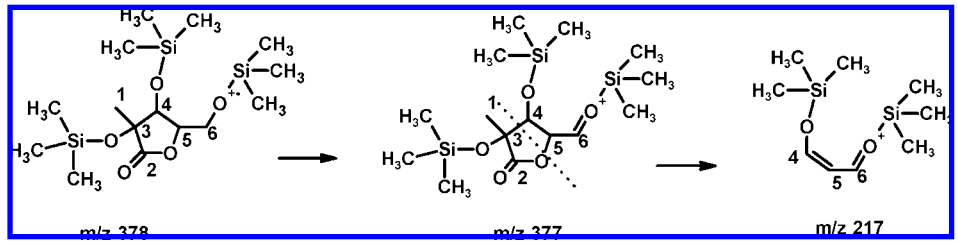

Figure 5. Proposed fragmentation of the parent ion at *m*/*z* 378 of 2-*C*-methyl-2,3,5-tris-*O*-(trimethylsilyl)-D-ribonic acid γ-lactone (**2**) to form an ion at *m*/*z* 217. The numbers indicate the positions of the glucose carbon atoms.

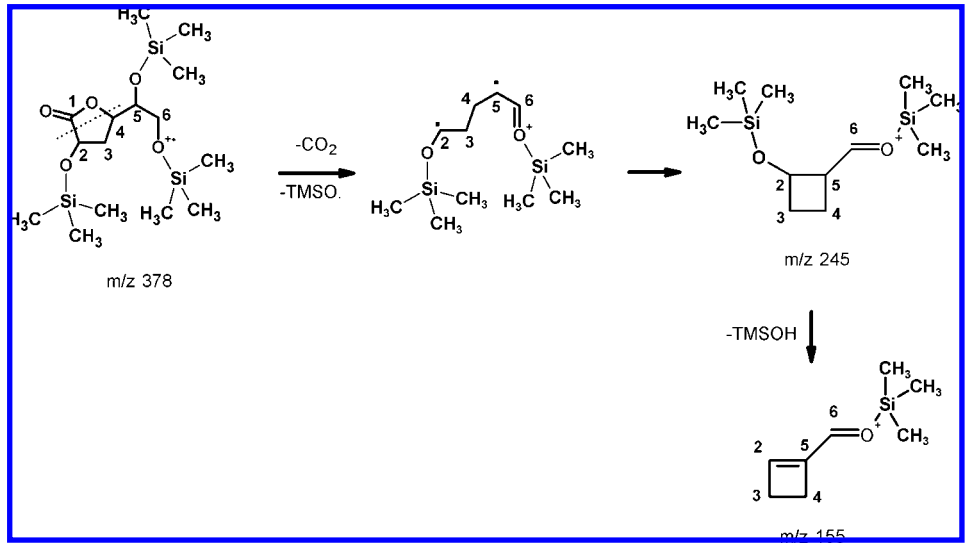

Figure 6. Proposed fragmentation of the parent ion at *m*/*z* 378 of 3-deoxy-2,5,6-tris-O-(trimethylsilyl)-D-ribo-hexonic acid lactone (**3**) to form an ion at *m*/*z* 155. The numbers indicate the positions of the glucose carbon atoms.

Table 5. Percent ^{13}C-Label[a] Distribution in Ion at *m*/*z* 217 of Ribonic Acid 2-*C*-Methyl-2,3,5-tris-*O*-(trimethylsilyl)-γ-lactone

	compound		
	M	**M + 1**	**M + 3**
D-glucose-U-$^{13}C_6$/glycine	0	0	100
D-glucose/glycine	100	0	0
D-glucose-6-^{13}C/glycine	0	100	0
D-glucose-5-^{13}C/glycine	0	100	0
D-glucose-4-^{13}C/glycine	0	100	0
D-glucose-3-^{13}C/glycine	100	0	0
D-glucose-2-^{13}C/glycine	100	0	0
D-glucose-1-^{13}C/glycine	100	0	0
D-glucose/glycine-1-^{13}C	100	0	0
D-glucose/glycine-2-^{13}C	100	0	0
D-glucose/glycine-^{15}N	100	0	0

[a] A similar label incorporation pattern was also observed in the absence of glycine.

Table 6. Percent ^{13}C-Label[a] Distribution in Ion *m*/*z* 155 and *m*/*z* 245 of 3-Deoxy-2,5,6-tris-O-(trimethylsilyl)-D-ribo-hexonic Acid Lactone

	compound		
	M	**M + 1**	**M + 5**
D-glucose-U-$^{13}C_6$/glycine	0	0	100
D-glucose/glycine	100	0	0
D-glucose-6-^{13}C/glycine	0	100	0
D-glucose-5-^{13}C/glycine	0	100	0
D-glucose-4-^{13}C/glycine	0	100	0
D-glucose-3-^{13}C/glycine	0	100	0
D-glucose-2-^{13}C/glycine	0	100	0
D-glucose-1-^{13}C/glycine	100	0	0
D-glucose/glycine-1-^{13}C	100	0	0
D-glucose/glycine-2-^{13}C	100	0	0
D-glucose/glycine-^{15}N	100	0	0

[a] A similar label incorporation pattern was also observed in the absence of glycine.

In principle, both acids or their lactones should be formed; however, only 2,3,5-tris-O-(trimethylsilyl)-D-arabinonic acid γ-lactone (5 in **Figure 2**) was identified with certainty in the model system. This lactone is formed by the incorporation of the glucose carbon atoms of C-2 to C-6, as confirmed by labeling studies (**Tables 2** and **3**), as well as by investigating the label incorporation in the mass spectral fragment at *m*/*z* 204 (**Figure 7** and **Table 7**).

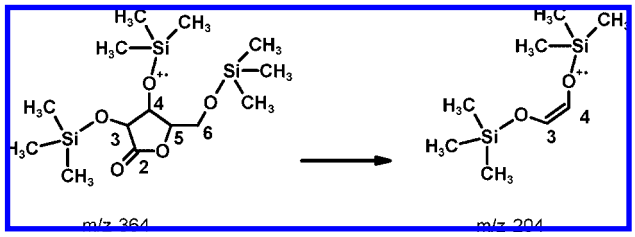

Figure 7. Proposed fragmentation of the parent ion at *m*/*z* 365 of 2,3,5-tris-*O*-(trimethylsilyl)-D-arabinonic acid γ-lactone (**5**) to form an ion at *m*/*z* 204. The numbers indicate the positions of the glucose carbon atoms.

Table 7. Percent ^{13}C-Label[a] Distribution in Ion at *m*/*z* 204 of 2,3,5-Tris-*O*-(trimethylsilyl)-D-arabinonic Acid γ-Lactone

	compound		
	M	M + 1	M + 2
D-glucose-U-$^{13}C_6$/glycine	0	0	100
D-glucose/glycine	100	0	0
D-glucose-6-^{13}C/glycine	0	0	0
D-glucose-5-^{13}C/glycine	0	0	0
D-glucose-4-^{13}C/glycine	0	100	0
D-glucose-3-^{13}C/glycine	0	100	0
D-glucose-2-^{13}C/glycine	0	0	0
D-glucose-1-^{13}C/glycine	100	0	0
D-glucose/glycine-1-^{13}C	100	0	0
D-glucose/glycine-2-^{13}C	100	0	0
D-glucose/glycine-^{15}N	100	0	0

[a] A similar label incorporation pattern was also observed in the absence of glycine.

The above studies performed under oxidative conditions have highlighted the ease of conversion of glucosone and its deoxy derivatives into aldonic and saccharinic acids or into their corresponding lactones. Furthermore, these studies indicate that oxidative conditions may deplete the Maillard reaction mixtures from important sugar dicarbonyls by converting them into their corresponding carboxylic acids, thus preventing the formation of many N-containing heterocyclic compounds important for flavor, aroma, or color.

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