Stereochemical Control of Maltol Formation in Maillard Reaction

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Maltol (3-hydroxy-2-methyl-4*H*-pyran-4-one) and HMF (hydroxymethylfurfural) are considered to be indicator compounds for the occurrence of 2,3- and 1,2-enolizations in solutions of reducing sugars. However, unlike HMF, maltol has been detected in the decomposition mixtures of reducing disaccharides, monosaccharide solutions containing amino acids but not in solutions of monosaccharides. On the other hand, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one can be detected in heated solutions of reducing monosaccharides alone, with no evidence of maltol formation; this intermediate therefore cannot be considered as the precursor of maltol. Evidently, maltol is formed in disaccharides through a different pathway than dehydration of 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one. Molecular modeling and energy-minimization studies using the MM2 force field have indicated that due to tautomeric shift, an unfavorable dihedral angle for E2 type of elimination of water and more favorable alternate reaction pathways prevent this pyranone from being converted into maltol under Maillard reaction conditions.

INTRODUCTION

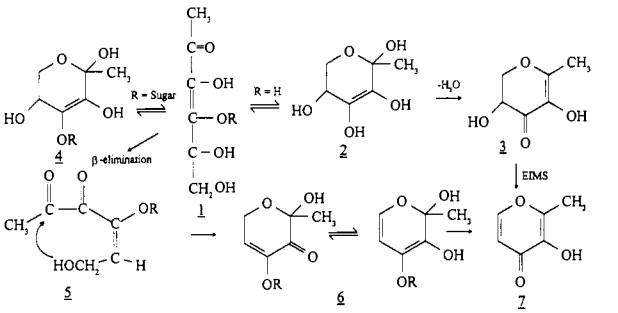
The enolization of reducing sugars and sugar derivatives under acid/base catalysis conditions initiates β-elimination reactions that eventually lead to the formation of reactive intermediates such as 1-deoxy-D-*erythro*-2,3-hexodiuloses (1 in Scheme 1, shown in the enol form) commonly known as 1-deoxyosone. This intermediate was shown to be formed from different hexoses (Feather and Harris, 1973) and from Amadori products of mono- and disaccharides (Beck et al., 1988) and is considered to be an important precursor in the formation of degradation products of sugars and Maillard model systems. It is assumed that they exist in cyclic hydroxyfuranones and hydroxypyranone (2) forms in solution. Intermediate 2, formed through monosaccharides, can produce 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (3) as a major product in all systems containing hexoses. At higher temperatures it decomposes, and it is suggested (Baltes et al., 1989) that it produces 2-hydroxy-3-methylcyclopenten-2-one. With disaccharides (R = glycosyl) 1 produces maltol (7). Under specific reaction conditions, pure 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one was found to be converted into maltol, hydroxymaltol, and isomaltol (Shaw et al., 1971). In order to elucidate the mechanism of maltol formation under Maillard reaction conditions, different reaction parameters that affect maltol formation were studied. In addition, different tautomeric forms of 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one were studied by molecular mechanics to determine their relative stabilities and molecular properties.

MATERIALS AND METHODS

All reagents and chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI). The synthesis of Amadori-proline was performed according to published procedures (Vernin et al., 1992).

Microwave Sample Preparation. A microwave digestion system, Model MDS 2000 (CEM Corp., Matthews, NC), which delivers 660 W of microwave power was used. The contents of 5 × 200 μL of 1 M sugar and/or 1 M amino acid solutions were deposited in a 250-μL tapered glass microvial (Hewlett-Packard, Palo Alto, CA) by successive evaporation of the water, using Speed Vac (Savant Corp., Farmingdale, NY). The vials were placed inside a Teflon PFA digestion vessel (CEM Corp.) together with 5.0 mL of water. The vessel cap was sealed using a Capping Station (CEM Corp.) and then connected to a surge trap and a manifold. The manifold had connections for evacuation, nitrogen purge, and pressure controlling and a safety release mechanism. The vessels were evacuated and purged six times with nitrogen gas. Then the vessels were placed on the turntable of the microwave unit, under positive nitrogen pressure. The manifold was switched to allow monitoring of the vessel pressure and control of microwave power using a pressure controller (CEM Corp.). The microwave unit was equipped with an inlet/outlet port to allow the tubing connected to the vessel and the pressure controller to pass through the cavity wall without allowing microwave leakage. The pressure controller was set to begin controlling the microwave power when the pressure in the vessel reached a specified value (20, 50, 60, 80, 110 psi) corresponding to temperatures of 110, 127, 134, 144, and >200 °C, respectively).

Scheme 1. Mechanism of Formation of Maltol and 2,3-Dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one



Sample Preparation. Sugar (0.1 g of monosaccharide/1 mL of water or 0.05 g of dissacharide/1 mL of water) solutions were heated in an open test tube at 150 °C for 10 min with and without α-alanine (0.1 g; total volume 1.5 mL) and at acidic or basic conditions (1.0 μL of either 1 N HCl or 1 N NaOH; when alanine was present 1.5 μL of either 1 N HCl or 1 N NaOH was added).

Amadori-Proline Systems. Amadori-proline (0.1 g) in 200 μL (1.8 M) was heated (150 °C for 10 min) alone and in the presence of either 0.1 g of alanine or 0.1 g of proline. The resulting solutions were extracted with a total volume of 1 mL of diethyl ether and concentrated to a final volume of 200 μL. Two microliters of this solution was injected into GC/MS for analysis.

GC/MS Analysis. A Hewlett-Packard GC/mass-selective detector (5890 GC/5971B MSD) was used for the analyses and

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Table 1. Normalized Percent Relative Areas of Maltol, HMF, and Pyranone Formed under Different pH Conditions from Heated Sugar Solutions at 150 °C for 10 min[a]

	fructose			palatinose		
	acid	base	neutral	acid	base	neutral
maltol	0	0	0	0	0	0
pyranone	4 (1.6)	64 (3)	6 (3.3)	0	0	0
HMF	96 (44)	36 (1.7)	94 (50)	100 (18.4)	0	100 (7)
	maltose			lactose		
	acid	base	neutral	acid	base	neutral
maltol	0	85 (1.7)	6 (1.1)	0	45 (1)	5 (0.7)
pyranone	0	0	0	0	0	0
HMF	100 (0.6)	15 (0.3)	94 (19)	100 (0.9)	55 (1.3)	95 (14)

[a] Values in parentheses are peak areas relative to the internal standard bipyridine. Maltol, 3-hydroxy-2-methyl-4*H*-pyran-4-one; HMF, (hydroxymethyl)furfural; pyranone, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one. Note: When the reactions were performed in the presence of an 8-fold excess of alanine, maltol, pyranone, and HMF were not detected in the reaction mixtures.

acquisition of the electron impact mass spectra. Two microliters of sample solutions were injected in a splitless mode into a fused silica capillary column (DB-1, 30-m length × 0.32-mm i.d. × 0.25-μm film thickness; Supelco, Inc.). The initial column temperature (70 °C) was increased after 5 min at a 5 °C/min rate and maintained at 250 °C for 12 min. Carrier gas (helium) flow rate was 0.85 cm³/min; injection port temperature was 250 °C; capillary direct MS interface temperature was 185 °C; ion source temperature was 280 °C; and the ionization voltage was 70 eV. The mass range was 33–350 amu, and electron multiplier voltage, 1500 V.

Energy Minimization. Energy-minimization studies were performed using MM2(87) force field, interfaced with Tripos Alchemy for Windows.

RESULTS AND DISCUSSION

Although maltol is assumed to be an important product of Maillard reaction, it has not been detected in appreciable amounts in most Maillard model systems. Small amounts of maltol have been detected in the thermal degradation mixtures of reducing and nonreducing disaccharides such as maltose, lactose, sucrose, and starch (Ito, 1977; Johnson, et al., 1969) but not in monosaccharide degradation mixtures, despite the fact that 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (3) is formed abundantly in these systems; this fact raises the question of whether compound 3 can be converted by dehydration into maltol. Shaw et al. (1971) have demonstrated that 3 can dehydrate only under very specific reaction conditions (thionyl chloride in pyridine). On the other hand, maltol has been detected in trace amounts in Maillard systems containing monosaccharides and amino acids or Amadori products (Mills and Hodge, 1976). It is evident that maltol is formed by different mechanisms depending on the starting carbohydrate and that 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one is very difficult to dehydrate into maltol under Maillard reaction conditions.

Effect of Sugar Type on Maltol Formation. Two reducing monosaccharides (fructose and glucose) and three reducing disaccharides (palatinose, maltose, and lactose) were investigated as to their potential for producing 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (pyranone), maltol, and HMF. The sugar solutions were heated under different pH conditions, in an open tube at 150 °C for 10 min, and the resulting mixtures were analyzed by GC/MS. The peak areas of the three indicated compounds were normalized, and percent relative values are summarized in Table 1. The results indicated that under acidic and neutral conditions, HMF formation is preferred relative to maltol and pyranone; in addition, maltol is formed under basic and neutral conditions only from disaccharides with free C-6 hydroxyl groups on the reducing sugar. Basic pH seems to increase the formation of maltol relative to neutral conditions. None of the disaccharides formed pyranone.

Table 2. Normalized Relative Percent Areas of Decomposition Produots of Fructose[a]

	110 °C (20 psi)		135 °C (60 psi)		145 °C (80 psi)	
	N_2	O_2	N_2	O_2	N_2	O_2
maltol	0	0	0	0	0	0
pyranone	11	10	13	10	14	9
HMF	89	90	87	90	86	91

[a] Fructose was microwaved at 20, 60, and 80 psi for 5 min under O_2 and N_2. The peak areas for pyranone, maltol, and HMF were normalized and relative percent areas reported. Maltol, 3-hydroxy-2-methyl-4*H*-pyran-4-one; HMF, (hydroxymethyl)furfural; pyranone, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one.

Table 3. Normalized Relative Percent Areas of Decomposition Products of Selected Monosaccharides and Maltose[a]

	tagatose		glucose		fructose		maltose	
	N_2	O_2	N_2	O_2	N_2	O_2	N_2	O_2
maltol	0	0	0	0	0	0	7	0
pyranone	20	0	4	2	11	6	0	0
HMF	80	100	96	98	89	94	93	0

[a] Tagatose, glucose, fructose, and maltose were microwaved at 50 psi for 5 min under air and nitrogen. The peak areas for maltol, pyranone, and HMF were normalized and relative percent areas reported. Maltol, 3-hydroxy-2-methyl-4*H*-pyran-4-one; HMF (hydroxymethyl)furfural; pyranone, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one.

Effect of Exclusion of Oxygen on the Decomposition of Fructose. The effect of excluding oxygen on the decomposition of fructose and possible formation of maltol was studied using the microwave sample preparation method described under Materials and Methods. Fructose was decomposed under nitrogen and air at three temperatures (110, 135, and 145 °C), and the amounts of HMF and pyranone formed were analyzed by GC/MS; the results are summarized in Table 2. According to the results obtained, maltol was not formed under either condition and both pyranone and HMF formation from fructose was not significantly affected by oxygen, which implies that their precursors are not susceptible to oxidative decomposition.

Effect of Exclusion of Oxygen on the Decomposition of Selected Sugars. In order to ascertain the effect of exclusion of oxygen on the formation of maltol, maltose, tagatose, fructos, and glucose were decomposed as above under nitrogen and air. Table 3 summarizes the results obtained. Tagatose and maltose seem to be more sensitive to oxygen relative to the monosaccharides studied (fructose and glucose). Exclusion of oxygen from the reaction mixture seems to enhance the formation of maltol and HMF from maltose. The effect of oxygen on HMF formation seems to depend on the sugar type; this might indicate more than one mechanism of HMF formation.

Formation of Maltol from Maltose: Effect of Temperature, Time, Amino Acid, and Oxygen. Maltose being the most efficient source of maltol, the effect of temperature, oxygen, time, and amino acid on the formation of maltol was studied using the microwave sample preparation method. The results summarized in Table 4 indicate that exclusion of oxygen, addition of amino acid, and increasing the time and temperature of the reaction increase the amount of maltol produced.

Table 4. Normalized Percent Relative Areas of Maltol and HMF Formed from Maltose[a]

	maltol	HMF
Effect of Nitrogen		
70 psi/30 min/alanine/O_2	91 (10)	9 (3)
70 psi/30 min/alanine/N_2	100 (60)	0 (0)
Effect of Amino Acid		
50 psi/15 min/O_2	0 (0)	100 (450)
50 psi/15 min/alanine/O_2	73 (1)	27 (1)
40 psi/3 h/O_2	4 (11)	96 (770)
50 psi/3 h/alanine/O_2	86 (19)	14 (9)
Effect of Temperature		
50 psi/15 min/alanine/O_2	73 (1)	27 (1)
75 psi/15 min/alanine/O_2	80 (2)	20 (1.5)
110 psi/15 min/alanine/O_2	89 (19)	11 (6)
50 psi/15 min/O_2	0 (0)	100 (450)
75 psi/15 min/O_2	3 (2.0)	97 (170)
110 psi/15 min/O_2	2 (5.5)	98 (8300)
Effect of Time		
70 psi/30 min/alanine/O_2	91 (10.5)	9 (3)
70 psi/60 min/alanine/O_2	89 (51)	11 (18)
70 psi/90 min/alanine/O_2	89 (100)	11 (35)

[a] Values in parentheses represent peak areas relative to the smallest peak area of maltol and HMF (indicated in bold). Maltol, 3-hydroxy-2-methyl-4*H*-pyran-4-one; HMF, (hydroxymethyl)furfural.

Proposed Mechanisms of Formation of Maltol. The fact that maltol has been detected in the decomposition mixtures of disaccharides and Amadori compounds but not in monosaccharide decomposition mixtures indicates that the logical precursor of maltol, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (**3**), cannot dehydrate efficiently to produce maltol and that there are different mechanisms of maltol formation depending on the reactants. Different experiments performed in this study have confirmed the fact that maltol could be formed through disaccharides and Amadori compounds and that monosaccharides could not produce maltol under different experimental conditions, including exclusion of air.

1. Formation of Maltol through Disaccharides. The proposed mechanism of maltol formation from disaccharides is shown in Scheme 1. Lack of maltol formation from maltose under acidic conditions and its increased formation under basic conditions (see Table 1) provide evidence that reducing disaccharides produce maltol through base-catalyzed 2,3-enolizations. In addition, lack of evidence for the formation of compound **4**, equivalent in structure to 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (**3**), in the decomposition mixtures of disaccharides indicates that intermediate **1** undergoes a different reaction to produce **6**, which has been detected in disaccharide solutions (Kramhöller et al., 1993). The fact that intermediate **6** can be formed under neutral conditions but requires basic pH for conversion into maltol (Kramhöller et al., 1993) suggests that compound **6** can be produced from **1** by a base-catalyzed β-elimination to produce **5** which then cyclizes through the C-6 hydroxyl group into pyranone **6**. Maltol formation is prevented when the C-6 hydroxyl group of the reducing disaccharide is substituted, as in the case of palatinose (see Table 1).

2. Factors That Prevent Conversion of 2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one into Maltol, under Maillard Reaction Conditions. The mechanism of formation of 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, through 2,3-enolization pathway of reducing monosaccharides as shown in Scheme 1, can explain the detection of this compound in all hexoses. 2,3-Dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one can be considered as an indicator compound for the occurrence of 2,3-enolization in simple hexoses as HMF is an indicator of

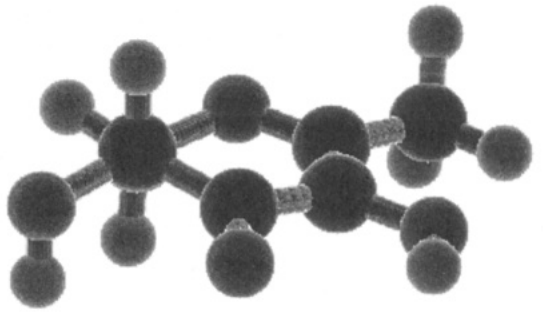
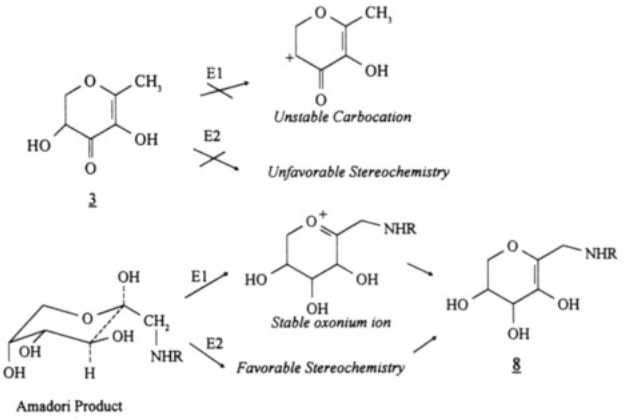


Figure 1. Energy-minimized structure of 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one.

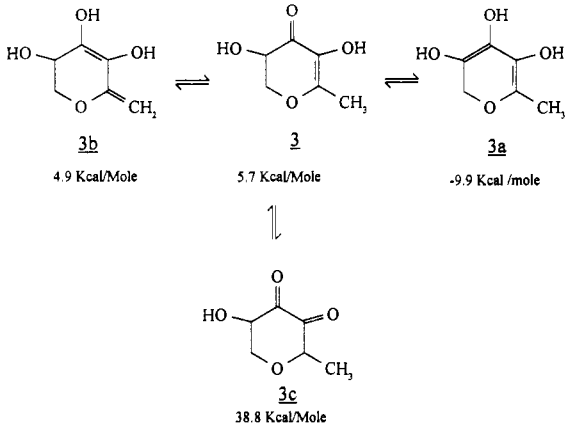
Scheme 2. Mechanisms of Dehydration



1,2-enolizations in most hexoses. However, there are no indications that pyranone **3** can dehydrate into maltol under Maillard reaction conditions, although it has been demonstrated that such dehydrations are possible under electron impact mass spectrometric (EIMS) conditions (Yaylayan et al., 1993). All attempts by Shaw et al. (1971) to dehydrate **3** under various conditions failed except when **3** was treated with thionyl chloride in pyridine which yielded maltol as the major product. In addition, **3** was found to rearrange into isomaltol in dichloromethane solution containing traces of hydrogen chloride and water, and in the presence of chromium trioxide/pyridine it was oxidized into hydroxymaltol. These facts indicate that there are energy barriers (high activation energy E_a) associated with such dehydrations, which usually proceeds through E1 type of mechanism. However, the intermediate carbocation that can be formed under E1 conditions, at the α-position to the carbonyl group, is destabilized through charge localization by the inductive effect of the carbonyl group (Scheme 2). An alternate mechanism of dehydration is the E2 type elimination reaction, which has a stereochemical requirement of antiperiplanar geometry of the hydroxyl group relative to the hydrogen (dihedral angle close to −180°). To estimate the HO–C–C–H dihedral angle of (*R*)-2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (**3**), the energy-minimized structure of this compound was generated (Figure 1) from the MM2 force field calculations which showed an dihedral angle of −54.5°. Hence, the dehydration reaction with E2 type mechanism will also require considerable energy of activation, since the four atoms involved in the transition state are not coplanar. Both E1 and E2 mechanisms are not favored due to structural and stereochemical effects (Scheme 2).

In addition to this energy barrier to dehydration, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one can exist in different tautomeric equilibria which can be initiated by enolization and ketonization reactions as shown in

Scheme 3. Tautomerization of 2,3-Dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one



Scheme 4. Oxidation of 2,3-Dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one

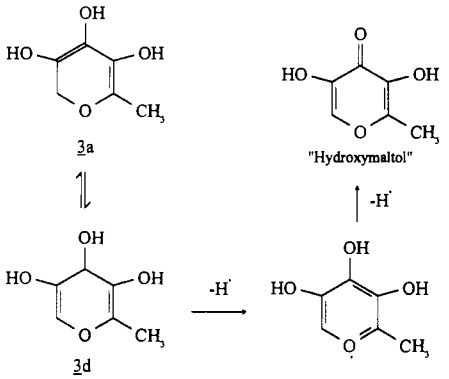


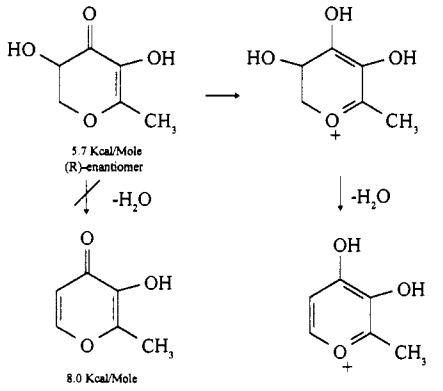
Table 5. GC/MS Chromatographic Peak Areas (×10⁶) of Pyranone, Hydroxymaltol, and Maltol Formed from Proline–Amadori Compound

system[a]	pyranone (3)	hydroxy-maltol	maltol (7)
proline–Amadori	40.0	19.8	trace
proline–Amadori + proline	97.2	47.6	trace
proline–Amadori + alanine	810.4	330.6	20.6

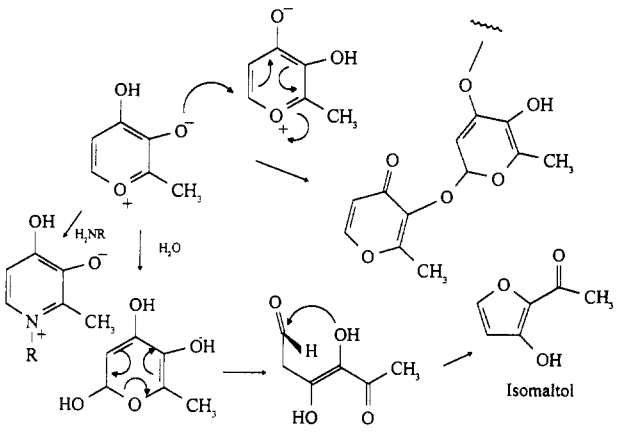
[a] HMF was not detected in these systems.

Scheme 3. The key tautomeric structures **3a–c** can exist in further tautomeric forms. The percent composition of different forms of pyranone **3** will be determined by the relative stability of each form. To estimate the stability of these tautomers, the total energy of the structures **3a–c** were minimized using the MM2 force field. The values obtained indicate that **3a** is the most stable tautomer and thus could contribute more to the tautomeric equilibrium. Furthermore **3a**, as shown in Scheme 4, can easily be oxidized to "hydroxymaltol" which has been detected in many Maillard model systems producing the pyranone including Amadori products. GC/MS analysis of decomposition (150 °C for 10 min) mixtures of proline–Amadori compound, for example, indicated the presence of, among others, two main products: the pyranone and hydroxymaltol (see Table 5). Addition of different amino acids to the Amadori product increased the concentration of pyranone with corresponding and proportional increase in hydroxymaltol concentration, indicating parent daughter relationship between the two products, as shown in Scheme 4. These observations are consistent with the predications of energy-minimization studies and with the results of Shaw et al. (1971). In addition, structures similar to pyranone **3**, in principle, can aromatize and form pyrylium ions (Balaban et al., 1982) as suggested in Scheme

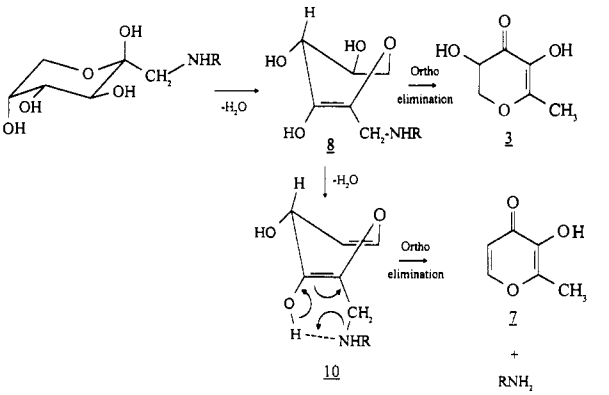
Scheme 5. Aromatization of 2,3-Dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one



Scheme 6. Proposed Reactions of Pyrylium Ions



Scheme 7. *Ortho*-Elimination Reactions of Amadori Compounds

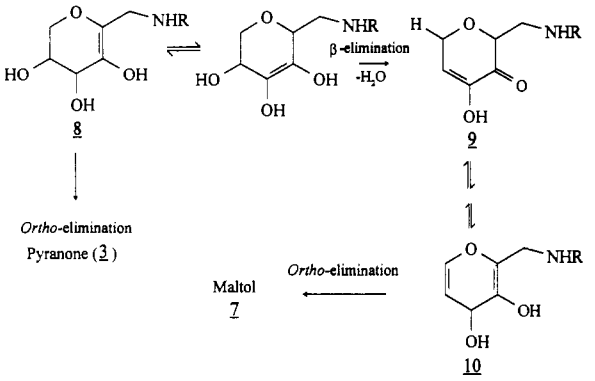


5. Pyrylium ions, once they are formed, can polymerize or react with O- and N-nucleophiles as proposed in Scheme 6 to produce pyrydinium betains and isomaltol among other heterocyclic compounds.

Therefore, energetic considerations, tautomeric shift, and favorable alternate reaction pathways prevent pyranone **3** from being dehydrated into maltol under Maillard reaction conditions.

3. Formation of Maltol through Amadori Product. Maltol has been detected in the decomposition mixtures of proline–Amadori products (Mills and Hodge, 1976). A mechanism has been proposed, though *ortho*-elimination, for the formation of maltol, on the basis of evidence from linked-field scan EIMS studies of different Amadori compounds (Yaylayan et al., 1991, 1993). Scheme 7 illustrates this process. Dehydration of Amadori compounds (Scheme 2) to produce **8** can proceed by either E1 or E2 type mechanisms or by a combination of the two. Formation of the stable oxonium ion can favor an E1 type

Scheme 8. Proposed Mechanism of Maltol and 2,3-Dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one Formation from Amadori Products



mechanism, and the antiperiplanar geometry of the anomeric hydroxyl group relative the C-3 hydrogen can facilitate an E2 type elimination (see Scheme 2). Intermediate **8** can either undergo an *ortho*-elimination to produce pyranone **3** or undergo a base-catalyzed β-elimination to produce **9** which is equivalent to structure **6** in Scheme 1. Subsequently compound **9** can undergo a series of enolizations to produce the hydroxypyran **10** which in turn can undergo another *ortho*-elimination to produce maltol (Scheme 8). This mechanism might also provide some explanation for the trace amounts of maltol detected relative to pyranone **3** in Amadori decomposition mixtures. In order to confirm the formation of maltol from Amadori products, aqueous solutions of proline–Amadori compound were decomposed alone and in the presence of free proline and alanine in separate experiments, at 150 °C for 10 min and the mixtures were extracted with ether and analyzed by GC/MS. The results indicated that maltol indeed was produced along with pyranone **3** from Amadori products (see Table 5).

Conclusion. Supporting evidence that maltol is formed directly from intact Amadori product, without passing through 2,3-enolization pathway, was presented, which was based on energy-minimization studies using an MM2 force field which indicted that the logical precursor of maltol, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (**3**), cannot dehydrate under Maillard reaction conditions to produce maltol due to stereochemical considerations.

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