

Glycerol, an Underestimated Flavor Precursor in the Maillard Reaction

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ABSTRACT: The objective of the present work was to investigate in depth the role of glycerol in Maillard reactions and its potential to act as an active flavor precursor. Reactions using isotopically labeled compounds (various reducing sugars, proline, and glycerol) unambiguously demonstrated that, in addition to its role of solvent, glycerol actively contributes to the formation of proline-specific compounds in Maillard model systems. Additionally, rhamnose and fucose/proline/glycerol systems generated the 2-propionyl-1(3),4,5,6-tetrahydropyridines, known for their roasty, popcorn aroma. Their formation from such systems is unprecedented. The results presented here have direct implications for flavor generation during thermal processing of foods containing glycerol, which is a ubiquitous food ingredient and an underestimated flavor precursor.

KEYWORDS: Maillard reaction, glycerol, flavor precursor, labeled reaction

INTRODUCTION

Maillard reaction systems based on L-proline are well-known to generate cooked rice or roasty cracker-like flavor.^{1–3} This aroma was attributed to the formation of 2-acetyl-1-pyrroline (2-AP) and 2-acetyl-1(3),4,5,6-tetrahydropyridines (2-ATHPs), two α -acetyl-cyclic enamines known for their low odor thresholds.^{4–6} They are ubiquitous in many natural sources such as pandan leaves^{7,8} and processed food products such as basmati rice,⁹ bread crust,¹⁰ toast,¹¹ popcorn,¹² and sweet corn based products.¹³ Additionally, α -acetyl-cyclic enamines have been generated in heated glucose/proline model systems.^{14–19} Previous studies using isotopically labeled compounds in glucose/proline model systems (silica gel, phosphate buffer 0.1 mol/L, 160 °C, 10 min) have shown that 2-AP and 2-ATHPs were generated from the condensation of 1-pyrroline, the Strecker degradation product of proline, and respectively the hydrated form of oxopropanal and hydroxy-2-propanone.¹⁷

Glycerol is a polyol compound widely used in the food industry as a humectant, solvent, filler in commercial low-fat foods, and thickening agent. It has been considered for a long time as an inert solvent and used as an a_w -adjusting agent in the Maillard reaction.^{20–23} Thus, Lu et al. observed the increase of volatiles generated by glucose and mono-, di-, or triglycine in aqueous glycerol (0–100%) and attributed the effect to the water content.²³ However, reactivity of glycerol in the Maillard reaction has been earlier postulated in nonenzymatic browning reactions,^{24–26} and recently the formation of [¹³C₃]-1-hydroxy-2-propanone was observed when fructose and alanine were heated in [¹³C₃]-glycerol and potassium phosphate buffer.²⁷

The purpose of the present work was to assess the role of glycerol as solvent and/or active precursor in the formation of proline-specific compounds in various Maillard model systems. Isotopically labeled reactants (glycerol, proline, glucose, and fucose) were used, and Carbon Module Labeling (CAMOLA) experiments were performed to identify transient intermediates and elucidate the formation of Maillard-type volatiles from labeling experiments and isotopomeric quantifications.²⁸

MATERIALS AND METHODS

Chemicals. Chemicals were obtained of analytical grade. Glycerol, L-rhamnose monohydrate (Rha), D-glucose (Glu), and D-xylose (Xyl) were purchased from Fluka. L-Fucose (Fuc) and [¹³C₃]-glycerol were from Aldrich. [1,6-¹³C₂]-D-Glucose, [¹³C₆]-D-glucose, and [U-¹³C₅]-proline were from Cambridge Isotope and [6-¹³C₁]-L-fucose, [3-¹³C₁]-L-fucose, and [U-¹³C₆]-L-fucose from Omicron. 2-AP and the 2-ATHPs were purchased from Toronton Research Chemicals.

Reactions with Sugar/Proline/Glycerol Systems. Proline (100 mg) and reducing sugar (10 mg) were added to glycerol (3400 mg) and water (Vittel, 600 μ L). The mixture was heated in a closed vessel for 1 h at 120 °C and then cooled to room temperature.

Reactions with Proline/Glycerol Systems. Proline (25 mg) was added to glycerol (850 mg) and water (Vittel, 150 μ L). The mixture was heated in a closed vessel for 1 h at 120 °C and then cooled to room temperature.

Reactions with Proline/50% [¹³C₃]-Glycerol System. Proline (25 mg) was added to glycerol (425 mg), labeled [¹³C₃]-glycerol (425 mg), and water (Vittel, 150 μ L). The mixture was heated in a closed vessel for 1 h at 120 °C and then cooled to room temperature.

Analysis. All samples were analyzed in duplicate or triplicate by headspace solid-phase microextraction in tandem with gas chromatography coupled to mass spectrometry (HS-SPME/GC-MS). The fiber (SPME fiber PDMS-DVB 65 μ m 23 gauge needle, Supelco 57345-U) was exposed for 10 min at 30 °C to the headspace above the samples. After sampling, the fiber was transported into the injector port in splitless mode at 250 °C for 5 min to desorb and transfer volatile compounds into the chromatographic column. The injector was equipped with a 0.75 mm i.d. liner (Supelco). GC separation was done on a HP-SMS column of 30 m length, 0.25 mm i.d., and 0.25 μ m film thickness (Agilent 19091S-433). The GC oven temperature program (Agilent Technologies 6890 GC oven) started at 30 °C during 3 min, was increased at 6 °C/min until 240 °C, and was held for 15 min. The GC was coupled to a MS (Agilent Technologies 5973) mass selective detector operating in EI/TIC (70 eV) mode. For the calculation of the

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isotopic proportions, the values were corrected by subtracting the naturally occurring percentages of ^{13}C in $\text{M}^+ + 1$.

RESULTS AND DISCUSSION

Sugar/Proline/Glycerol Systems: Initial Screening of Sugars. Reactions of proline and selected sugar (rhamnose, glucose, fucose, and xylose) were performed in aqueous glycerol (85%). After heating for 1 h at 120 °C, the volatile fraction was analyzed by HS-SPME/GC-MS. Table 1

Table 1. Main Volatile Compounds Formed during Heating of “Sugar/Proline/Glycerol” Systems

compound ^a	RI	no sugar	Glu	Rha	Fuc	Xyl
1-pyrroline ^b	668	x	x	x	x	x
2-acetyl-1-pyrroline	919	x	x	x	x	x
1-(1-pyrrolidinyl)-2-propanone ^b	1017		x	x	x	x
2-acetylpyridine ^b	1029	x	x	x	x	x
2-acetyl-3,4,5,6-tetrahydropyridine	1044	x	x	x	x	x
2-acetyl-1,4,5,6-tetrahydropyridine	1139	x	x	x	x	x
2-propionyl-3,4,5,6-tetrahydropyridine ^b	1143			x	x	
2-propionyl-1,4,5,6-tetrahydropyridine ^b	1234			x	x	

^aIdentification confirmed by GC retention index and mass spectra of authentic compounds. ^bTentatively identified by matching mass spectra library and internal database of retention indices.

summarizes the proline-specific compounds present in the different sugar/proline/glycerol systems. 1-Pyrroline, 2-AP, 2-ATHPs, 1-(1-pyrrolidinyl)-2-propanone, and 2-acetylpyridine were found in all sugar/proline/glycerol systems. Except for 1-pyrroline, the Strecker degradation product of proline, all compounds are known for their characteristic roasted and popcorn-like aroma. 2-Acetylpyridine was previously found in peptide/glucose systems,²⁹ in roasted peanuts,^{30,31} in hot air popped popcorn,³² and in Xiangjing-8618 rice and Yahnokao-luo leaves.³³ 1-(1-Pyrrolidinyl)-2-propanone has been previously identified in various proline/sugar and proline/1,3-dihydroxyacetone model systems.^{4,14} Interestingly, 2-propionyl-1(3),4,5,6-tetrahydropyridines (2-PTHPs) were exclusively formed with fucose (6-deoxy-L-galactose) and rhamnose (6-deoxy-L-mannose). 2-PTHPs have been detected in fresh popcorn,¹² Iberian ham,³⁴ peanut seed oil,³⁵ and in a Chinese plant called *Semnostachya menglaensis* Tsui.³⁶ They have been also generated in heated and buffered glucose/proline model systems by Hofmann et al.,¹⁸ but their formation in such fucose or rhamnose/proline/glycerol systems had not been reported so far.

Proline/Glycerol System. Quite surprisingly, we observed during our investigation that 1-pyrroline, 2-AP, 2-ATHPs, and 2-acetylpyridine were also formed in simple proline/glycerol, therefore clearly indicating that the presence of a reducing sugar is not required to form these volatiles in such reaction systems containing glycerol (Table 1). Isotopically labeled glycerol and proline were thus used to clarify the role of each reactant in the formation of proline-specific compounds. As shown in Table 2, when [$^{13}\text{C}_5$]-proline was reacted with glycerol and water, only the [$^{13}\text{C}_4$]-2-AP and [$^{13}\text{C}_4$]-2-ATHPs were formed. Mechanistically, this is in accordance with previous literature data and confirmed that 1-pyrroline, formed

Table 2. Proportion of Isotopomers from the Reaction between [$^{13}\text{C}_5$]-Proline and Glycerol/Water (1 h, 120 °C)

compound ^a	proportion of labeled carbon atoms in the molecule (%)						
	RI	m/z	0	1	2	3	4
1-pyrroline ^b	668	69	0	0	0	0	100
2-acetyl-1-pyrroline	919	111	0	0	0	0	100
2-acetylpyridine ^b	1026	121	0	0	0	0	100
2-acetyl-3,4,5,6-tetrahydropyridine	1044	125	0	0	0	0	100
2-acetyl-1,4,5,6-tetrahydropyridine	1139	125	0	0	0	0	100

^aIdentification confirmed by GC retention index and mass spectra of authentic compounds. ^bTentatively identified by matching mass spectra library and internal database of retention indices.

from the Strecker degradation of proline, is the key common precursor of 2-AP and 2-ATHPs.¹⁷

When proline was heated in a mixture of 50/50 [$^{13}\text{C}_3$]-labeled and unlabeled glycerol, 42% of [$^{13}\text{C}_2$]-2-AP and respectively 45 and 42% of [$^{13}\text{C}_3$]-2-ATHPs were generated (Table 3). Incorporation of ^{13}C -carbons in α -acetyl-cyclic

Table 3. Proportion of Isotopomers from the Reaction between Proline, [$^{13}\text{C}_3$]-Glycerol, and Glycerol/Water (1 h, 120 °C)

compound ^a	proportion of labeled carbon atoms in the molecule (%)						
	RI	m/z	0	1	2	3	4
1-pyrroline ^b	668	69	100	0	0	0	0
2-acetyl-1-pyrroline	919	111	54	4	42	0	0
2-acetylpyridine ^b	1026	121	54	0	0	46	0
2-acetyl-3,4,5,6-tetrahydropyridine	1044	125	50	0	5	45	0
2-acetyl-1,4,5,6-tetrahydropyridine	1139	125	47	0	11	42	0

^aIdentification confirmed by GC retention index and mass spectra of authentic compounds. ^bTentatively identified by matching mass spectra library and internal database of retention indices.

enamines proves unambiguously the active role of glycerol in their formation. Results of labeled reactions were in accordance with the accepted mechanism of formation of α -acetyl-cyclic enamines.¹⁷ Four carbons stem from the proline, confirming the role of the 1-pyrroline as key common precursor, and other carbons derive from glycerol (2 and 3 carbons in 2-AP and 2-ATHPs, respectively). Oxopropanal and hydroxy-2-propanone, the other precursors of α -acetyl-cyclic enamines, might be generated from glycerol according to the mechanisms described in Figure 1. During the heating process and in the presence of air, glycerol might be oxidized into dihydroxyacetone, which then can lose a molecule of water to form the oxopropanal. Hydroxy-2-propanone might be formed via the Strecker degradation of proline and oxopropanal but also by direct dehydration of glycerol.

Glucose/Proline/Glycerol System Using Isotopically Labeled Reactants. Reactions with labeled glucose and unlabeled proline/glycerol were then performed to better assess the actual contribution of glucose in flavor generation and gain further insight on mechanisms involved in the formation of 2-AP and 2-ATHPs in such ternary systems. [$^{13}\text{C}_6$]-Glucose was reacted with proline in glycerol/water. The

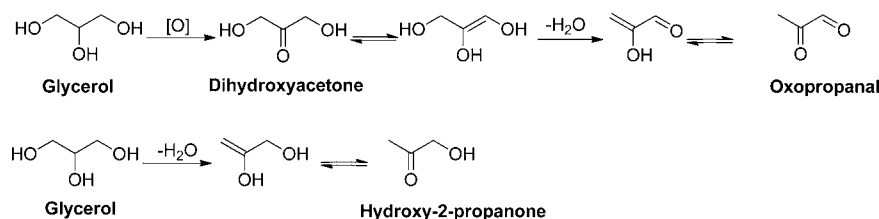


Figure 1. Proposed mechanism to form oxopropanal and hydroxy-2-propanone from glycerol. Black dots represent labeled carbons.

Table 4. Proportion of Isotopomers from the Reaction between [$^{13}\text{C}_6$]-Glucose, Proline, and Glycerol/Water (1 h, 120 °C)

compound ^a	RI	m/z	proportion of labeled carbon atoms in the molecule (%)				
			0	1	2	3	4
1-pyrroline ^b	668	69	100	0	0	0	0
2-acetyl-1-pyrroline	919	111	38	4	58	0	0
2-acetylpyridine ^b	1026	121	100	0	0	0	0
2-acetyl-3,4,5,6-tetrahydropyridine	1044	125	79	0	4	17	0
2-acetyl-1,4,5,6-tetrahydropyridine	1139	125	76	0	7	16	0

^aIdentification confirmed by GC retention index and mass spectra of authentic compounds. ^bTentatively identified by matching mass spectra library and internal database of retention indices.

proportion of 2-AP and 2-ATHPs isotopomers after heating treatment is given in Table 4. Thirty-eight percent of 2-AP was not labeled and consequently did not derive from a glucose fragment. The levels of unlabeled 2-ATHPs were high (79 and 76%), meaning that the majority of these compounds in fact originated from the glycerol. [$^{13}\text{C}_1$]-2-AP (4%) and [$^{13}\text{C}_2$]-2-ATHPs (4 and 7%) were also detected and might be formed from recombination between glycerol fragments and labeled glucose fragments. Finally, 58% of [$^{13}\text{C}_2$]-2-AP and 16–17% of [$^{13}\text{C}_2$]-2-ATHPs were generated using [$^{13}\text{C}_6$]-glucose. These results therefore indicate that oxopropanal and hydroxy-2-propanone, the precursors of 2-AP and 2-ATHPs, originate in such systems from two different precursors, namely, glycerol and glucose. To deepen our investigation on 2-AP and 2-ATHPs formation from glucose, [1,6- $^{13}\text{C}_2$]-glucose was reacted with proline in glycerol/water. As shown in the Table 5, only one ^{13}C -carbon was incorporated to the 2-AP and 2-ATHPs after heat treatment. Forty-eight percent of 2-AP was ^{13}C -

Table 5. Proportion of Isotopomers from the Reaction between [1,6- $^{13}\text{C}_2$]-Glucose, Proline, and Glycerol/Water (1 h, 120 °C)

compound ^a	RI	m/z	proportion of labeled carbon atoms in the molecule (%)				
			0	1	2	3	4
1-pyrroline ^b	668	69	100	0	0	0	0
2-acetyl-1-pyrroline	919	111	52	48	0	0	0
2-acetylpyridine ^b	1026	121	100	0	0	0	0
2-acetyl-3,4,5,6-tetrahydropyridine	1044	125	81	19	0	0	0
2-acetyl-1,4,5,6-tetrahydropyridine	1139	125	82	18	0	0	0

^aIdentification confirmed by GC retention index and mass spectra of authentic compounds. ^bTentatively identified by matching mass spectra library and internal database of retention indices.

labeled, that is, slightly less than in the previous reaction with [$^{13}\text{C}_6$]-glucose (Table 4). Thus, oxopropanal that exclusively stems from glucose was mostly formed from carbons C1 or C6 of glucose, but a small fraction could also come from degradation/recombination reactions between unlabeled glycerol fragments and unlabeled sugar fragments (involving carbons C2–C5). The percentage of unlabeled ATHPs was similar to those obtained with [$^{13}\text{C}_6$]-glucose (79 and 76% vs 81 and 82%), meaning that hydroxy-2-propanone that derived from glucose was formed only from fragments including carbon C1 or C6. The results of these labeled experiments were in line with mechanisms proposed by Hofmann et al. and Hayami explaining the formation of effective carbonyl compounds from labeled glucose (Figure 2).^{17,37} Retroaldolization cleavage of the 1-deoxyosone, formed from glucose under Maillard-type conditions, could lead to hydroxy-2-propanone and dihydroxypropanal, which form oxopropanal after loss of water. Moreover, in the presence of high levels of proline in the medium, oxopropanal could also react with the amino acid and give the hydroxy-2-propanone (Strecker degradation). However, the concept of retroaldolization has been recently challenged,^{38,39} and hydroxy-2-propanone might be rather formed by isomerization of 1-deoxyosone followed by hydrolytic β -cleavage (Figure 2).³⁷ The current experimental data do not support either pathway.

Fucose/Proline/Glycerol System Using Isotopically Labeled Reactants. In addition to 2-AP and 2-ATHPs, fucose or rhamnose in the glycerol/proline system generated 2-PTHPs after thermal processing (Table 1). Proline and hydroxy-2-butanone have been proposed as precursors of 2-PTHPs in glucose/proline systems.¹⁸ The formation of the α -propionyl-cyclic enamines from fucose and rhamnose has not been described so far, and therefore we took the opportunity to further investigate mechanisms involved in their formation using isotopically labeled fucose because rhamnose was not available as a labeled compound.

As shown in Table 6, when a [$^{13}\text{C}_6$]-fucose/proline/glycerol system was heated, 52% of [$^{13}\text{C}_2$]-2-AP was detected, which is similar to the reaction with [$^{13}\text{C}_6$]-glucose (Table 4). The 2-ATHPs were found only unlabeled, suggesting that in the fucose/proline/glycerol systems, the hydroxy-2-propanone might be generated only from glycerol. On the contrary, 100% [$^{13}\text{C}_4$]-2-PTHPs were formed, confirming that their precursor, hydroxy-2-butanone, solely derives from fucose.

Additional labeled reactions were then performed with [6- $^{13}\text{C}_1$]- and [3- $^{13}\text{C}_1$]-fucose (Tables 7 and 8, respectively). No labeled 2-ATHP was found in either case, which is in accordance with the results obtained with [$^{13}\text{C}_6$]-fucose (Table 6). 2-AP was 100% unlabeled when [6- $^{13}\text{C}_1$]-fucose was used, meaning that oxopropanal is not formed from the fucose fragment including the carbon C6. Reaction with [3- $^{13}\text{C}_1$]-fucose led to 11% of [$^{13}\text{C}_1$]-2-AP, which is lower than the reaction with [$^{13}\text{C}_6$]-fucose (Table 6). This suggests that

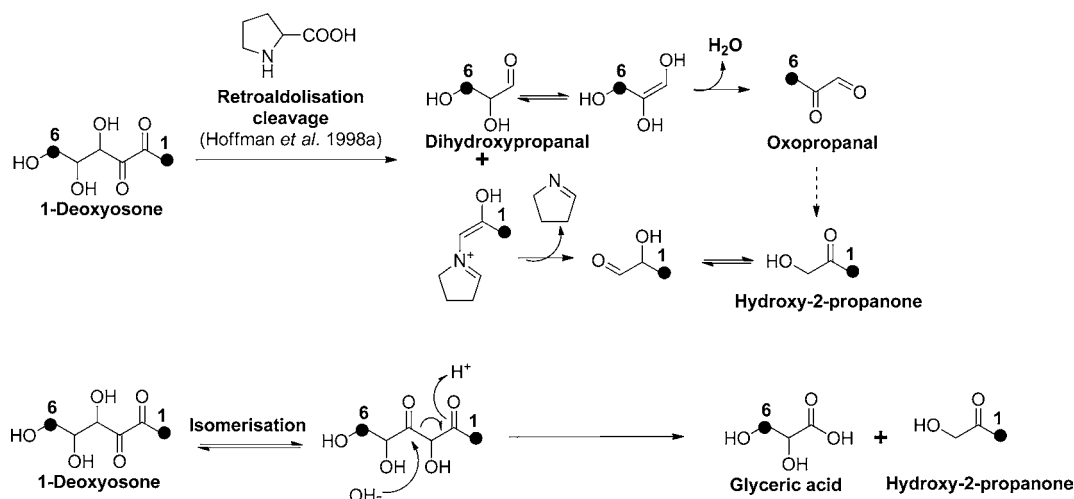


Figure 2. Postulated mechanisms to form oxopropanal and hydroxy-2-propanone from 1-deoxyosone. Black dots represent labeled carbons.

Table 6. Proportion of Isotopomers from the Reaction between [$^{13}\text{C}_6$]-Fucose, Proline, and Glycerol/Water (1 h, 120 °C)

compound ^a	proportion of labeled carbon atoms in the molecule (%)						
	RI	m/z	0	1	2	3	4
1-pyrroline ^b	668	69	100	0	0	0	0
2-acetyl-1-pyrroline	919	111	48	0	52	0	0
2-acetylpyridine ^b	1026	121	100	0	0	0	0
2-acetyl-3,4,5,6-tetrahydropyridine	1044	125	100	0	0	0	0
2-acetyl-1,4,5,6-tetrahydropyridine	1139	125	100	0	0	0	0
2-propionyl-3,4,5,6-tetrahydropyridine ^b	1143	139	0	0	0	0	100
2-propionyl-1,4,5,6-tetrahydropyridine ^b	1234	139	0	0	0	0	100

^aIdentification confirmed by GC retention index and mass spectra of authentic compounds. ^bTentatively identified by matching mass spectra library and internal database of retention indices.

Table 7. Proportion of Isotopomers from the Reaction between [$6\text{-}^{13}\text{C}_1$]-Fucose, Proline, and Glycerol/Water (1 h, 120 °C)

compound ^a	proportion of labeled carbon atoms in the molecule (%)						
	RI	m/z	0	1	2	3	4
1-pyrroline ^b	668	69	100	0	0	0	0
2-acetyl-1-pyrroline	919	111	100	0	0	0	0
2-acetylpyridine ^b	1026	121	100	0	0	0	0
2-acetyl-3,4,5,6-tetrahydropyridine	1044	125	100	0	0	0	0
2-acetyl-1,4,5,6-tetrahydropyridine	1139	125	100	0	0	0	0
2-propionyl-3,4,5,6-tetrahydropyridine ^b	1143	139	0	100	0	0	0
2-propionyl-1,4,5,6-tetrahydropyridine ^b	1234	139	0	100	0	0	0

^aIdentification confirmed by GC retention index and mass spectra of authentic compounds. ^bTentatively identified by matching mass spectra library and internal database of retention indices.

carbon C3 is involved in the formation of precursor but through a minor pathway. Finally, reactions of [$6\text{-}^{13}\text{C}_1$]- and

Table 8. Proportion of Isotopomers from the Reaction between [$3\text{-}^{13}\text{C}_1$]-Fucose, Proline, and Glycerol/Water (1 h, 120 °C)

compound ^a	proportion of labeled carbon atoms in the molecule (%)						
	RI	m/z	0	1	2	3	4
1-pyrroline ^b	668	69	100	0	0	0	0
2-acetyl-1-pyrroline	919	111	89	11	0	0	0
2-acetylpyridine ^b	1026	121	100	0	0	0	0
2-acetyl-3,4,5,6-tetrahydropyridine	1044	125	100	0	0	0	0
2-acetyl-1,4,5,6-tetrahydropyridine	1139	125	100	0	0	0	0
2-propionyl-3,4,5,6-tetrahydropyridine ^b	1143	139	0	100	0	0	0
2-propionyl-1,4,5,6-tetrahydropyridine ^b	1234	139	0	100	0	0	0

^aIdentification confirmed by GC retention index and mass spectra of authentic compounds. ^bTentatively identified by matching mass spectra library and internal database of retention indices.

[$3\text{-}^{13}\text{C}_1$]-fucose with proline and glycerol generated 100% [$^{13}\text{C}_1$]-2-PTHPs in both cases, meaning that hydroxy-2-butanone, the precursor of 2-PTHPs, exclusively originates from the fragmented fucose including the carbons C3 and C6. A possible mechanism of formation of hydroxy-2-butanone is proposed in Figure 3. Under Maillard conditions, the fucose (or rhamnose) might be cleaved and provide 2,3-dihydroxybutanal, which then might lead to oxobutanal after a loss of water. In the presence of a high level of proline in the medium, oxobutanal could react with the amino acid and give finally hydroxy-2-butanone (Strecker degradation).

In summary, reactions with isotopically labeled compounds unambiguously demonstrated that, in addition to its role of solvent, glycerol actively contributes to the formation of 2-AP and 2-ATHPs in both sugar/proline/glycerol and proline/glycerol systems. The formation of effective precursors of 2-AP and 2-ATHPs from glycerol would be explained by oxidation and dehydration of glycerol during heat treatment under air atmosphere. Interestingly, rhamnose and fucose/proline/glycerol systems generated 2-PTHPs, the higher homologues of 2-ATHPs. Their formation from such systems has not been described in previous work, and labeled reactions have allowed

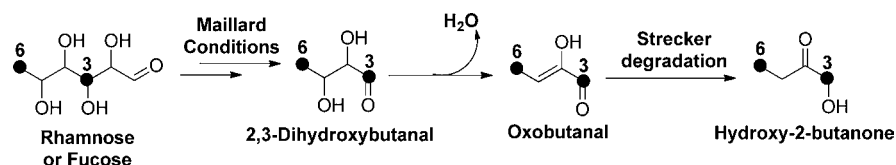


Figure 3. Proposed mechanism to form hydroxy-2-butanone from rhamnose and fucose. Black dots represent labeled carbons.

insight to be gained into the formation of the key precursor (hydroxy-2-butanone) from fucose and rhamnose.

The work reported here clearly indicates that the role of glycerol as flavor precursor has been largely underestimated so far. Given the ubiquitous occurrence of glycerol in industrial food products, our observations have direct implications for flavor generation during thermal processing of foods containing glycerol (e.g., bakery and savory products). Preliminary works in our laboratories also indicate that this active role of flavor precursor is not restricted to glycerol but that other alkane polyols may behave similarly. These further developments will be reported at a later stage.

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Notes

The authors declare no competing financial interest.

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