*J. Agric. Food Chem.* **1994**, *42*, 2519–2524 **2519**

# Pyrolysis/GC/MS Analysis of 1-[(2′-Carboxy)pyrrolidinyl]-1-deoxy-D-fructose (Proline Amadori Compound)

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Pyrolysis/GC/MS was applied to the study of primary and secondary pyrolysis products of 1-[(2′-carboxy)pyrrolidinyl]-1-deoxy-D-fructose (proline Amadori compound). The Amadori product was pyrolyzed on a ribbon probe at 150, 200, 250, 300, an 350 °C for 10 s. The main products formed under these conditions were 1-(1′-pyrrolidinyl)-2-propanone, 2-hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one, and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one in addition to acetic acid and pyrrolidine. To produce secondary pyrolysis products, the Amadori compound was pyrolyzed at 250 °C in a quartz tube for 20 s; 14 secondary pyrolysis products were identified. The majority of the products were also reported to be formed during autoclaving of proline/monosaccharide mixtures at 150 °C for 1.5 h in water. In addition, the pyrolysis of D-glucose/proline and the proline Amadori compound was compared.

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**Keywords:** *Pyrolysis; proline; Amadori compound; decomposition; mechanism; Maillard reaction*

## INTRODUCTION

The reaction of proline with reducing monosaccharides and a variety of carbonyl compounds has been investigated extensively (Tressl et al., 1985a–c, 1989, 1990, 1993), and most of the proline-specific products have been isolated from model systems autoclaved at 150 °C for 1.5 h in water and subsequently extracted with diethyl ether and analyzed by GC/MS and characterized by independent synthesis. Such studies have indicated that proline can produce under Maillard reaction condition 2,3-dihydro-1*H*-pyrrolizines (Tressl et al., 1985a), pyrrolidine and piperidine derivatives (Tressl et al., 1985b), 2-(1-pyrrolidinyl)-2-cyclopentanones and cyclopent[*b*]azepin-8-(1*H*)-ones (Tressl et al., 1985c), 2-(2′-furyl)pyrrolidines and 2-(2′-furyl)piperidines (Helak et al., 1989a), and 7*H*-cyclopenta[*b*]pyridin-7-ones (Helak et al., 1989b). Mills and Hodge (1976) studied the vacuum thermolysis of the proline Amadori compound heated at 140 and 240 °C for 3.5 h. The major products found in the distillate at 140 °C were six-carbon-containing dehydration products of the sugar moiety, whereas at 240 °C the Amadori compound yielded more pyrrolidine derivatives, pyrrolidine amides, an 2-pyrrolino-substituted furans. Yaylayan et al. (1993) demonstrated by linked-field scan studies that under electron impact mass spectrometric conditions the principal fragmentation pathway leads to the formation of pyrrolidine, proline, and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one.

The temperature and the mode of decomposition of Amadori compounds influence the type and distribution pattern of the products formed. Pyrolysis of Amadori products, coupled to GC/MS (Py/GC/MS), can provide a fast and convenient method of studying the effect of temperature on the decomposition products and generating, at the same time, pyrograms that can be used as fingerprints for specific Amadori products. Lapolla et al. (1992) applied Py/GC/MS to study the products arising from the interaction of glucose with polylysine to identify diagnostic markers for the advanced glycation reaction.

**Table 1. Major Compounds Identified by Py/GC/MS[a] from Proline Amadori and Proline/Glucose Mixtures, Pyrolyzed for 20 s at 250 °C**

| retention time (min) | compound |
|---|---|
| 6.5 | acetic acid (**1**) |
| 8.5 | pyrrolidine (**2**) |
| 12.3 | 1-(1′-pyrrolidinyl)-2-propanone (**3**) |
| 13.4 | 3-(1′-pyrrolidinyl)-2-butanone (**4**) |
| 14.1 | 1-(1′-pyrrolidinyl)-2-butanone (**5**) |
| 15.2 | 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**6**) |
| 15.9 | *N*-acetylpyrrolidine (**7**) |
| 16.4 | *N*-propanoylpyrrolidine (**8**) |
| 16.5 | 1-(5′-methylfurfuryl)pyrrolidine (**9**) |
| 17.2 | *N*-butanoylpyrrolidine (**10**) |
| 19.7 | 2,5-dimethyl-4-(1-pyrrolidinyl)-3(2*H*)-furanone (**11**) |
| 20.1 | 5-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one (**12**) |
| 20.8 | 7-methyl-2,3,4,5,6,7-hexahydrocyclopent[*b*]azepin-8(1*H*)-one (**13**) |
| 21.3 | 1-[5′-(hydroxymethyl)furfuryl]pyrrolidine (**14**) |
| 21.6 | 2-hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one (**15**) |
| 23.6 | maltoxazine (**16**) |
| 27.8 | proline dimer (**17**) |
| 29.9 | 5-methyl-2,3-bis(1′-pyrrolidinyl)-2-cyclopenten-1-one (**18**) |

[a] Fused silica DB-5 column, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness; Supelco, Inc.

Pyrolysis can be performed at various temperatures, with different temperature programs. Different techniques of sample introduction, such as application of the sample on a ribbon probe (platinum filament) as a solution or as a solid in a quartz tube inserted inside the coil probe, can provide valuable information regarding the differences between the initial and the advanced pyrolysis products. On the ribbon probe, the pyrolysis products are swept away as soon as they are formed by the carrier gas into the GC column, without undergoing further secondary reactions. On the other hand the

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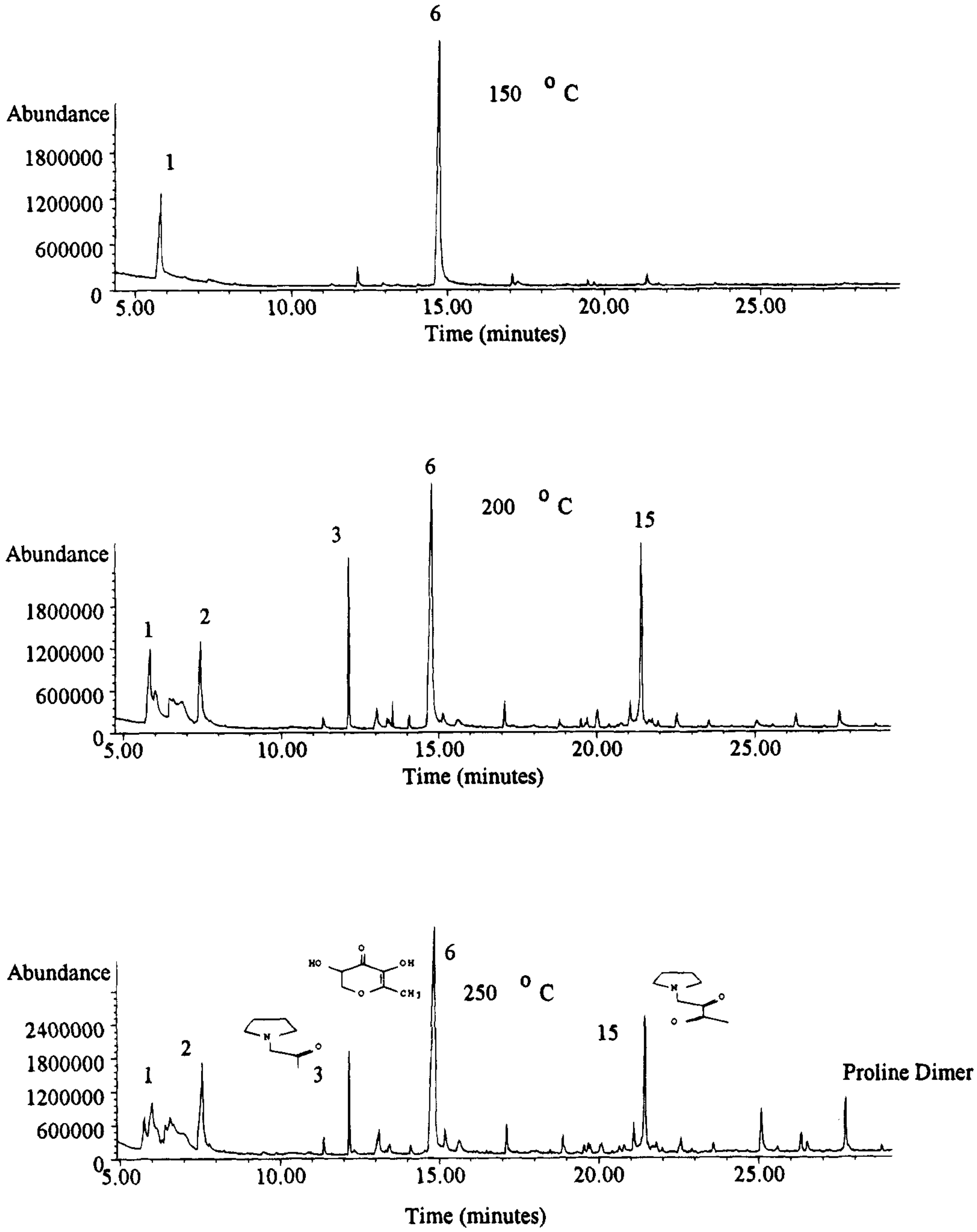


**Figure 1.** Pyrograms of proline Amadori compound using the ribbon probe at different temperatures for 10 s. Peaks: (1) acetic acid; (2) pyrrolidine; (3) 1-(1′-pyrrolidinyl)-2-proipanone; (6) 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one; (15) 2-hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one; proline dimer 3,9-diazatricyclo[7.3.0.0*.3*.7*]dodecane-2,8-dione.

pyrolysis products produced in the quartz tube should migrate from the sample to the hotter regions of the pyrolyzer, and this may initiate additional fragmentation and produce secondary products by further reactions (Irwin, 1982). In this paper, we demonstrate that Py/GC/MS can be used to identify primary and secondary pyrolysis products of the proline Amadori compound with minimum sample preparation and analysis time [10–20 s of total heating time (THT) and 35 min of chromatographic run time] and that the pyrolysis of the proline Amadori compound in the quartz tube for 20 s at 250 °C is comparable to the autoclaving of a proline/glucose mixture at 150 °C for 1.5 h in water.

## 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).

**Pyrolysis/GC/MS Analysis.** A Hewlett-Packard GC/mass selective detector (5890 GC/5971B MSD) interfaced to a CDS Pyroprobe 2000 unit was used for the Py/GC/MS analysis. Two modes of sample introduction were used: (a) 1 mg equivalent of sample dissolved in methanol/water (70:30) was applied on the platinum filament with a THT of 10 s or (b) 1–5 mg solid samples were introduced inside the quartz tube (0.3 mm thickness) and plugged with quartz wool and inserted inside the coil probe with a THT of 20 s. The GC column flow rate was 0.8 mL/min for a split ratio of 92:1 and a septum purge of 3 mL/min. The Pyroprobe interface was set at the temperature at which the sample was to be pyrolyzed, and the Pyroprobe was set at the desired temperature at a rate of 50 °C/ms. Capillary direct MS interface temperature was 180 °C; ion source temperature was 280 °C. The ionization voltage was 70 eV, and the electron multiplier was 1494 V. The mass range analyzed was 35–350 amu. The column was a fused

**Table 2. Relative Percent Areas of Major Products Identified in Different Model Systems**

| system[a] | 6[b] | 15[c] | 3[d] | acetic acid | pyrrolidine | total |
|---|---|---|---|---|---|---|
| ARP$^{150}$ R | 69.0 | 2.0 | 2.5 | 22.9 | 0.0 | 96.4 |
| ARP$^{200}$ R | 26.7 | 13.3 | 6.2 | 7.8 | 7.2 | 61.2 |
| **ARP$^{250}$ R** | **23.4** | **8.8** | **3.1** | **7.9** | **8.3** | **51.5** |
| ARP$^{300}$ R | 15.4 | 14.5 | 4.5 | 9.2 | 8.7 | 52.3 |
| ARP$^{350}$ R | 12.7 | 13.0 | 3.6 | 10.7 | 10.2 | 50.2 |
| **ARP$^{250}$ T** | **13.6** | **5.9** | **3.4** | **7.0** | **9.5** | **39.4** |
| GluPro$^{250T}$ | 15.4 | 3.0 | 1.9 | 11.2 | 13.6 | 45.1 |
| Glu$^{250T}$ | 12.7 | 0.0 | 0.0 | 0.0 | 0.0 | 12.7 |
| proline$^{250T}$ | 0.0 | 0.0 | 0.0 | 0.0 | 2.0 | 2.0 |

[a] R, ribbon pyrolysis (10 s); T, quartz tube pyrolysis (20 s); ARP, proline amadori product; Pro, proline; Glu, glucose. [b] 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**6**). [c] 1-(1′-Pyrrolidinyl)-2-propanone (**3**). [d] 2-Hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one (**15**).

silica DB-5 column (30 m length × 0.25 mm i.d. × 0.25 μm film thickness; Supelco, Inc.). The column initial temperature was −5 °C for 3 min and was increased to 50 °C at a rate of 30 °C/min; immediately the temperature was further increased to 270 °C at a rate of 8 °C/min and kept at 270 °C for 5 min. Products that were not found in the mass spectral libraries were identified by comparison with literature mass spectral data.

## RESULTS AND DISCUSSION

To elucidate the mechanistic events leading to primary and secondary pyrolysis products, the proline Amadori compound was pyrolyzed both on a ribbon probe and in a quartz tube. The products identified in the latter are listed in Table 1, and those identified from ribbon pyrolysis experiments are listed in Table 2.

**Pyrolysis of Proline Amadori Compound on the Ribbon Probe—Primary Pyrolysis Products.** A solution of proline Amadori compound dissolved in methanol/water was deposited on the ribbon and heated sequentially, first to remove the solvent and subsequently to pyrolyze the product. A fast flow rate of carrier gas, combined with short THT (10 s) was used to sweep the initial pyrolysis products into the GC column without extensive secondary product formation. The Amadori product was pyrolyzed at 150, 200, 250, 300, and 350 °C. Figure 1 shows the pyrograms at 150, 200, and 250 °C. The main products formed at these conditions were 1-(1′-pyrrolidinyl)-2-propanone (**3**), 2-hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one (**15**), and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**6**) in addition to acetic acid and pyrrolidine. At temperatures higher than 200 °C, relatively small amounts of secondary pyrolysis products were also formed. Table 2 lists the relative percent areas of the major products at all temperatures studied. At 150 °C more than 96% of the total peak area is represented by the five initial products; this percentage drops to about 60% at 200 °C and remains around 50% between 250 and 350 °C.

**Pyrolysis of Proline Amadori Compound in the Quartz Tube—Secondary Pyrolysis Products.** To induce the formation of secondary pyrolysis products, solid samples of Amadori product of sugar/amino acid mixtures (1−5 mg) were introduced into the center of a quartz tube and both sides were plugged with glass wool. The samples were pyrolyzed using the coil probe. Longer total heating time (20 s) allows more secondary pyrolysis products to be formed. To elucidate the origin of various products formed, proline, glucose, an equimolar mixture of proline and glucose, and equimolar mixture of proline and glyceraldehyde, and the proline Amadori compound were pyrolyzed at 250 °C. The main product formed from the pyrolysis of proline alone was 3,9-diazatricyclo[7.3.0.0*.3*.7*]dodecane-2,8-dione (proline dimer), a cyclic diamide (98% of the total peak area); the remaining 2% was the pyrrolidine. Table 3 lists the pyrolysis products of glucose identified by GC/MS. More than 77% of the total chromatographic peak area was represented by furfural, (hydroxymethyl)furfural (HMF), and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**6**). More than 18 peaks were produced. Pyrolysis of an equimolar amount of glucose/proline mixture produces a very similar pyrogram to that of the proline Amadori compound as shown in Figure 2. The pyrolysis products that could be identified in both systems are shown in Table 1. Products that were not found in the spectral libraries were identified by comparison with literature mass spectral data and are listed in Table 4.

**Table 3. Major Compounds Identified by Py/GC/MS[a] from Glucose, Pyrolyzed for 20 s at 250 °C**

| retention time (min) | compound | % area |
|---|---|---|
| 6.4 | acetic acid | 3.5 |
| 8.5 | furfural | 18.7 |
| 13.5 | furancarboxylic acid methyl ester | 2.5 |
| 15.2 | 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one | 12.7 |
| 16.7 | HMF | 46 |
| 21.4 | butanoic acid | 3.2 |

[a] Fused silica DB-5 column, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness; Supelco, Inc.

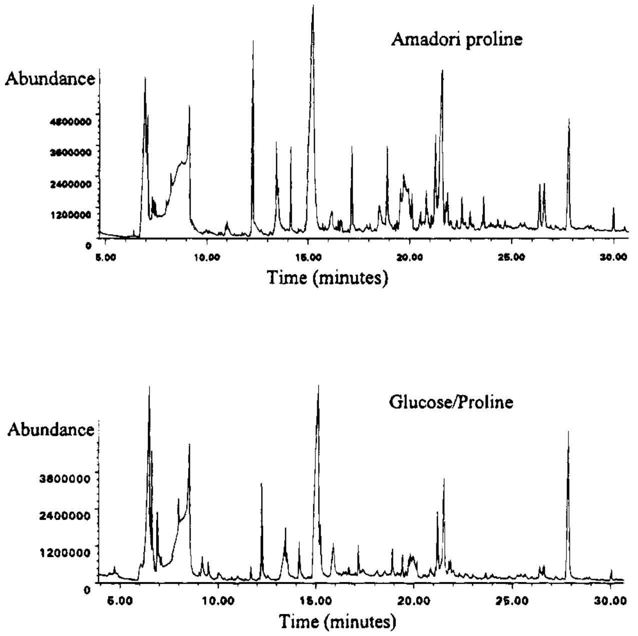


**Figure 2.** Pyrograms of proline Amadori compound and proline/glucose mixture using the quartz tube at 250 °C for 20 s.

**Comparison of Pyrolysis of Proline Amadori Compound and Proline/Glucose Mixture.** Inspection of Figure 2 indicates that under pyrolysis conditions (250 °C, 20 s) the proline/glucose mixture rapidly produces Amadori compound as evidenced by the striking similarity between their pyrograms. In addition, the lack of free glucose pyrolysis products in the pyrogram of the proline/glucose mixture indicates the efficiency of Amadori rearrangement under pyrolysis conditions. Under the same pyrolysis conditions phenylalanine/glucose and Amadori phenylalanine show similar behavior. However, pyrolysis of a glycine/glucose mixture shows more free glucose pyrolysis products, and fewer glycine Amadori products, indicat-

**Table 4. Mass Spectrometric Data Compared to Literature Values**[a]

**1-(1′-pyrrolidinyl)-2-propanone (3)**
127(2), 85 (06), **84** (**100**), 82 (2), 56 (07), 55 (20), 54 (3), 43 (07), 42 (43), 41 (07)
[a]127 (2), 85 (06), **84** (**100**), 82 (2), 56 (06), 55 (18), 54(3), 43 (07), 42 (31), 41 (04)

**3-(1′-pyrrolidinyl)-2-butanone (4)**
99 (23), **98** (**100**), 70 (9), 69 (8), 56 (29), 55 (12), 43 (12), 42 (15)
[a]99 (07), **98** (**100**), 70 (3), 69 (5), 56 (23), 55 (08), 43 (07), 42 (06)

**1-(1′-pyrrolidinyl)-2-butanone (5)**
141 (1), 110 (0), 95 (0), **84** (**100**), 70 (1), 69 (0), 57 (1), 56 (3), 55 (10), 42 (22), 41 (4)
[a]141 (1), 110 (3), 95 (8) **84** (**100**), 70 (3), 69 (5), 57 (1), 56 (3), 55 (08), 42 (17), 41 (3)

**1-(5′-methylfurfuryl)pyrrolidine (9)**
165 (22), 164 (11), 122 (6), 96 (7), **95** (**100**), 83 (6)
[a]165 (20), 164 (09), 122 (6), 96 (8), **95** (**100**), 83 (6)

**2,5-dimethyl-4-(1-pyrrolidinyl)-3(2*H*)-furanone (11)**
**181** (**100**), 166 (18), 138 (55), 124 (89), 110 (65), 98 (90), 82 (33), 70 (19), 55 (51), 54 (26), 43 (85)
[a]**181** (**100**), 166 (17), 138 (49), 124 (84), 110 (69), 98 (90), 82 (30), 70 (19), 55 (47), 54 (23), 43 (76)

**5-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one (12)**
165 (91), 164 (28), 150 (56), 136 (08), **122** (**100**), 108 (19), 95 (29), 94 (28), 70 (29), 67 (26), 54 (25)
[a]165 (90), 164 (28), 150 (27), 136 (40), **122** (**100**), 108 (38), 95 (41), 94 (34), 70 (23), 67 (24), 54 (25)

**7-methyl-2,3,4,5,6,7-hexahydrocyclopent[*b*]azepin-8(1*H*)-one (13)**
**165** (**100**), 164 (54), 150 (17), 137 (58), 136 (51), 122 (52), 109 (36), 108 (57), 95 (19), 94 (38), 81 (31), 80 (29), 67 (32), 55 (41), 54 (23), 53 (27)
[a]**165** (**100**), 164 (32), 150 (20), 137 (33), 136 (43), 122 (83), 109 (51), 108 (62), 95 (70), 94 (46), 81 (29), 80 (28), 67 (59), 55 (24), 54 (24), 53 (34)

**1[5′-(hydroxymethyl)furfuryl]pyrrolidine (14)**
181 (45), 180 (28), 150 (46), **111** (**100**), 84 (15), 81 (13), 42 (16)
[a]181 (46), 180 (28), 150 (42), **111** (**100**), 84 (20), 81 (14), 42 (19)

**2-Hydroxy-1-(1′-pyrrolidiyl)-1-buten-3-one (15)**
155 (72), 138 (10), 137 (12), 126 (8), 112 (96), **84** (**100**), 83 (27), 70 (74), 57 (14), 56 (30), 55 (41), 43 (66), 42 (50)
[a]155 (67), 138 (09), 137 (11), 126 (7), 112 (97), **84** (**100**), 83 (26), 70 (64), 57 (11), 56 (24), 55 (36), 43 (52), 42 (55)

**5-methyl-2,3-bis(1′-pyrrolidinyl)-2-cyclopenten-1-one (19)**
**234** (**100**), 219 (6), 206 (42), 205 (18), 193 (28), 191 (66), 179 (15), 177 (16), 163 (31), 150 (19), 136 (24), 122 (24), 110 (15), 109 (16), 108 (18), 96 (38), 94 (18), 82 (13), 81 (17), 70 (41), 68 (23), 55 (32), 44 (08), 41 (48)
[a]**234** (**100**), 219 (7), 206 (59), 205 (21), 193 (43), 191 (82), 179 (16), 177 (17), 163 (32), 150 (14), 136 (55), 122 (23), 110 (13), 109 (16), 108 (14), 96 (33), 94 (13), 82 (13), 81 (14), 70 (69), 68 (29), 55 (37), 44 (31), 41 (55)

[a] Tressl et al. (1985a–c).

ing that glycine decomposes more quickly than it reacts with glucose under the experimental conditions. These preliminary data show that for relatively stable amino acids, pyrolysis of a mixture of the amino acid and glucose could give a good indication of the range of products that could be produced by the pyrolysis of the corresponding Amadori product.

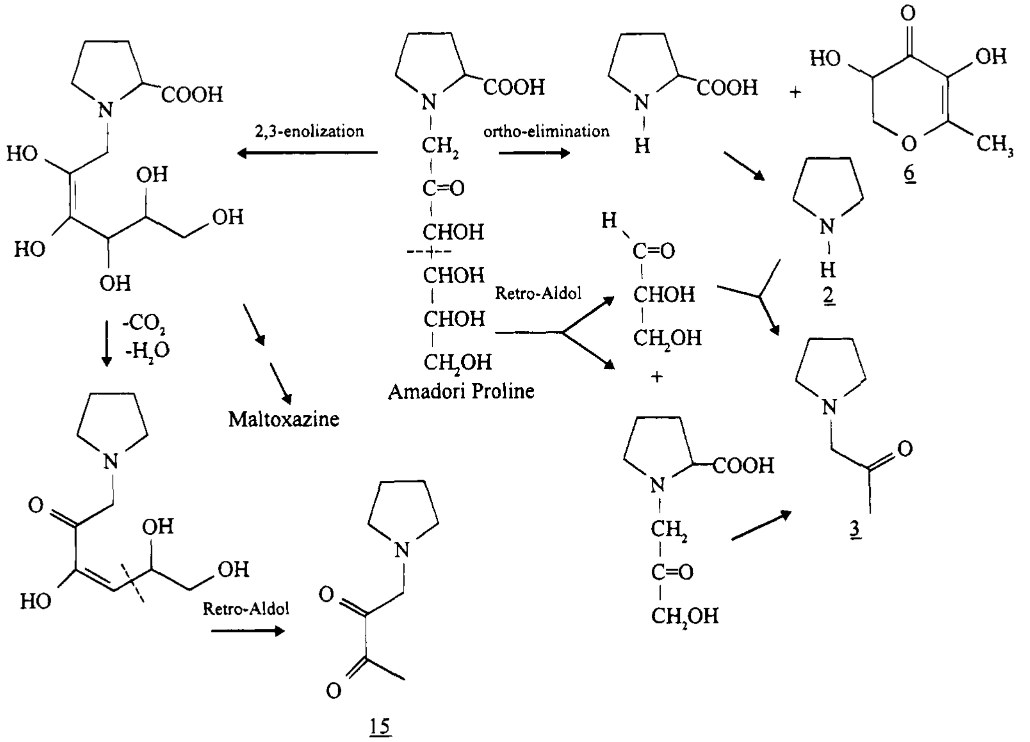
**Table 5. Formation Efficiencies ($\times 10^{13}$) Expressed as Gas Chromatographic Peak Areas per Mole of Starting Material**

| system[a] | maltoxazine | 6[b] | 15[c] | 3[d] | proline dimer |
|---|---|---|---|---|---|
| ARP$^{150}$ R | 0.00 | 6.4 | 0.2 | 0.2 | 0.04 |
| ARP$^{200}$ R | 0.10 | 6.9 | 3.5 | 1.6 | 0.4 |
| **ARP$^{250}$ R** | **1.10** | **9.1** | **3.5** | **1.2** | **1.0** |
| ARP$^{300}$ R | 0.20 | 6.4 | 6.0 | 1.8 | 1.0 |
| ARP$^{350}$ R | 0.25 | 6.5 | 6.6 | 1.8 | 1.2 |
| **ARP$^{250}$ T** | **0.34** | **5.7** | **3.6** | **2.2** | **3.2** |
| GluPro$^{250T}$ | 0.18 | 8.0 | 3.4 | 1.9 | 0.9 |
| Glu$^{250T}$ | 0.00 | 1.0 | 0.0 | 0.0 | 0.0 |
| Pro$^{250T}$ | 0.0 | 0.0 | 0.0 | 0.0 | 92.3 |

[a] R, ribbon pyrolysis (10 s); T, quartz tube pyrolysis (20 s). [b] 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyrane-4-one (**6**). [c] 2-Hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one (**15**). [d] 1-(1′-Pyrrolidinyl)-2-propanone (**3**).

Inspection of Table 2 indicates that the five major products identified during pyrolysis on the ribbon probe still comprise 39% of the total peak area of the pyrolysate of the Amadori product and around 45% of the total peak area of the pyrolysate of the glucose/proline mixture. Although glucose/proline mixtures produce products similar to that of proline Amadori compound, the efficiency of formation of proline-specific compounds is higher with the Amadori product. Table 5 expresses the ability of each model system studied to produce selected products as gas chromatographic peak areas per mole of the starting material. The Amadori product forms 1-(1′-pyrrolidinyl)-2-propanone (**3**), 2-hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one (**15**), and maltoxazine more efficiently than the corresponding proline/glucose mixture, but 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**6**) is formed more efficiently by the mixture due to the ability of glucose alone to produce this compound. Comparison of the formation efficiencies at 250 °C for the pyrolysis of Amadori compound using ribbon and coil probes also confirms our earlier assertion that in the quartz tube the formation of secondary pyrolysis products and bimolecular interactions are encouraged. Dimerization of proline is certainly a bimolecular reaction, and consequently the formation efficiency is increased 3.2 times in the quartz tube as opposed to the ribbon pyrolysis. Similarly, the formation efficiency of 1-(1′-pyrrolidinyl)-2-propanone (**3**) increased relative to ribbon pyrolysis, indicating a bimolecular interaction. However, maltoxazine and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**6**) formation efficiencies did not increase but instead dropped due to their thermal instability, as indicated by their reduced efficiency of formation at 300 and 350 °C on the ribbon probe. On the other hand, the formation efficiency of 2-hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one (**15**) was not changed in either mode of pyrolysis, and it is thermally stable, as evidenced by its increased formation at 300 and 350 °C. This indicates a direct

**Scheme 1. Proposed Pyrolysis Fragmentation Mechanism of Proline Amadori Product**



formation from intact Amadori product similar to maltoxazine and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**6**). Scheme 1 illustrates the proposed initial mechanistic events leading to the pyrolysis of proline Amadori compound. Carbon–nitrogen bond cleavage through ortho-elimination (Yaylayan and Mandeville, 1994a) seems to be a prominent reaction, producing free proline and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**6**). Similar initial fragmentation patterns for proline Amadori compound were also observed under electron impact conditions (Yaylayan et al., 1993). Proline produced from this initial fragmentation can dimerize or decarboxylate to produce pyrrolidine, which subsequently reacts with glyceraldehyde (formed through retro-Aldrich reaction of proline Amadori compound) through Amadori rearrangement to produce 1-(1′-pyrrolidinyl)-2-propanone (**3**) after β-elimination and reduction steps. The latter can also be produced by the remaining fragment of the Amadori product, after β-elimination followed by decarboxylation and reduction steps. When a mixture of proline and glyceraldehyde was pyrolyzed under the same conditions as those of proline Amadori compound, 1-(1′-pyrrolidinyl)-2-propanone (**3**) was one of the main products formed. In addition, proline Amadori compound can undergo thermally catalyzed 2,3-enolization to produce maltoxazine (Yaylayan and Mandeville, 1994b) and 2-hydroxy-1-(1′-pyrrolidinyl)-1-buten-3-one (**15**), from intact Amadori product, after a retro-Aldol reaction, as proposed in Scheme 1.

**Conclusion.** Py/GC/MS can be a fast and convenient technique for the analysis of Maillard reaction products arising from the Amadori intermediate, especially with amino acids that are stable enough under pyrolysis conditions to react with the sugar rather than decompose.

## ACKNOWLEDGMENT

V.Y. acknowledges funding for this research by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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Received for review June 16, 1994. Accepted August 25, 1994.⊗

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⊗ Abstract published in *Advance ACS Abstracts*, October 1, 1994.