ELSEVIER

Food Chemistry 74 (2001) 1–9

Food Chemistry

www.elsevier.com/locate/foodchem

Elucidation of the mechanism of pyrrole formation during thermal degradation of ^{13}C-labeled L-serines

Varoujan A. Yaylayan *, Anahita Keyhani

McGill University, Department of Food Science and Agricultural Chemistry 21,111 Lakeshore,
Ste. Anne de Bellevue, Quebec, Canada H9X 3V9

Received 3 May 2000; accepted 6 December 2000

Abstract

Pyrolysis of [^{13}C-1], [^{13}C-2] and [^{13}C-3]-labelled L-serines generated mono-substituted methyl and ethyl derivatives of pyrroles and pyrazines among other compounds. Analyses of label incorporation into the pyrroles have indicated their formation through aldol condensation of acetaldehyde with different α-aminocarbonyl compounds followed by cyclization and loss of water (Knorr pyrrole synthesis). Comparison of the label incorporation patterns of the α-aminocarbonyls involved in the formation of methyl and ethyl-substituted pyrroles with that of similarly substituted pyrazines, revealed their common origin. In addition, α-aminocarbonyls involved in the formation of 2- and 3-substituted pyrroles had identical label distribution patterns, indicating their formation through the same carbonyl precursors. Furthermore, the major pathway (55%) leading to the formation of the α-aminocarbonyl precursors of methyl-substituted pyrroles involved aldol addition of formaldehyde to glycolaldehyde, whereas the only pathway leading to the formation of the α-aminocarbonyl precursors of ethyl-substituted pyrroles involved the interaction of alanine — formed in situ — with glycolaldehyde. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Maillard reaction mechanisms; ^{13}C-labeled L-series: py/GC/MS; Pyrroles; Pyrazines; Acetaldehyde; Glycolaldehyde

1. Introduction

Thermal degradation of L-serine alone (180–360°C) has been reported to produce a wide range of heterocyclic compounds, such as methyl and ethyl-substituted pyrazines and pyrroles, pyrrolylalkanols and some fused heterocyclic compounds (Kato, Kurata, Ishitsuka & Fujimaki 1970; Reese & Baltes, 1992; Wang & Odell, 1973). Kato et al. (1970) pyrolyzed L-serine at 280°C and identified several methyl and ethyl-substituted pyrazines and pyrroles in addition to ethylamine, ammonia, ethanolamine, acetaldehyde and 2,5-diketo-3,6-dimethylpiperazine. Wang and Odell (1973) similarly identified various pyrazines when L-serine was pyrolyzed at 200°C. According to Baltes and Bochmann (1987) the thermal degradation of an equimolar mixture of L-serine and L-threonine produced around 32% pyrazines and 25% pyrroles. More detailed studies on the degradation products of L-serine were carried out by Reese and Baltes (1992). They autoclaved L-serine at 120, 150 and 180°C for 1 h, however, only at 150 and 180°C could degradation products be detected. The number of products increased from 58 to 70 at the higher temperature. In addition to methyl and ethyl-substituted pyrazines and pyrroles, they also detected 2-(1-pyrrolyl)-ethanol, pyrrolo[1,2-a]pyrazine and various simple carbonyl, dicarbonyl and α-hydroxycarbonyl compounds. The origin of such reactive carbonyl intermediates formed upon thermal degradation of amino acids and sugars is relatively difficult to determine without ^{13}C-labelling studies, due to the multiple origin of these components. By utilizing pyrolysis/gas chromatography/mass spectrometry (Py-GC/MS) to generate and identify stable end-products, such as pyrazines formed by the incorporation of these reactive intermediates into their molecular structure using properly ^{13}C-labeled reactants, identification of their origin becomes possible (Yaylayan & Keyhani, 1998; Yaylayan, Keyhani & Huyghues-Despointe,

---

* Corresponding author. Tel: +1-514-398-7918; fax: +1-514-398-7977

E-mail-address: yaylayan@macdonald.mcgill.ca (V.A. Yaylayan).

PII: S0308-8146(00)00332-0

1998). Using such an approach Yaylayan, Keyhani and Wnorowski, (2000) have identified, based on labelling studies, the mechanism of formation of methyl-substituted pyrazines and the origin of sugar-specific reactive intermediates in L-serine degradation products. In this study, using variously ^{13}C-labelled L-serines, the origin of methyl and ethyl-substituted pyrroles was elucidated.

2. Materials and methods

All reagents and chemicals were purchased from Aldrich Chemical Company (Milwaukee, WI). DL-[2-^{13}C]alanine (92%), [2-^{13}C]glycine (98%) L-[1-^{13}C]serine (99%), L-[2-^{13}C]serine (99%), L-[3-^{13}C]serine (98%) were purchased from Cambridge Isotope Laboratories (Andover, MA).

2.1. Pyrolysis-GC/MS analysis

A Hewlett-Packard GC/mass selective detector (5890 GC/5971B MSD, Palo Alto, CA) interfaced to a CDS pyroprobe 2000 unit (Oxford, PA) was used for the Py-GC/MS analysis. Solid samples (1–4 mg) of ^{13}C-labelled L-serines were introduced inside a quartz tube (0.3 mm thickness) which was plugged with quartz wool and inserted inside the coil probe. The pyroprobe was set at the desired temperature (250°C) at a heating rate of 50°C/ms and with a total heating time (THT) of 20 s. The pyroprobe interface temperature was set at 250°C. 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. 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 1682 V. The mass range analyzed was 30–300 amu. The column was a fused silica DB-5 column (60 m length×0.25 mm i.d.×25 um film thickness; Supelco, Inc.). The column initial temperature (−5°C) was increased to 260°C at a rate of 10°C/min. and held at 260°C for 15 min.

3. Results and discussion

3.1. Conversions and thermal degradation

In a previous study (Yaylayan et al., 2000) using [^{13}C-1], [^{13}C-2] and [^{13}C-3]-labelled L-serines, we have identified three initial degradation pathways of L-serine (**a**, **b** and c in Fig. 1). Decarboxylation, followed by deamination, produces ethanolamine and acetaldehyde; a retro-aldol pathway generates formaldehyde and glycine. Dehydration of L-serine can lead to the formation of pyruvic acid, which eventually can be converted into the amino acid alanine or can decarboxylate to form acetaldehyde. Formation of alanine and glycine was confirmed

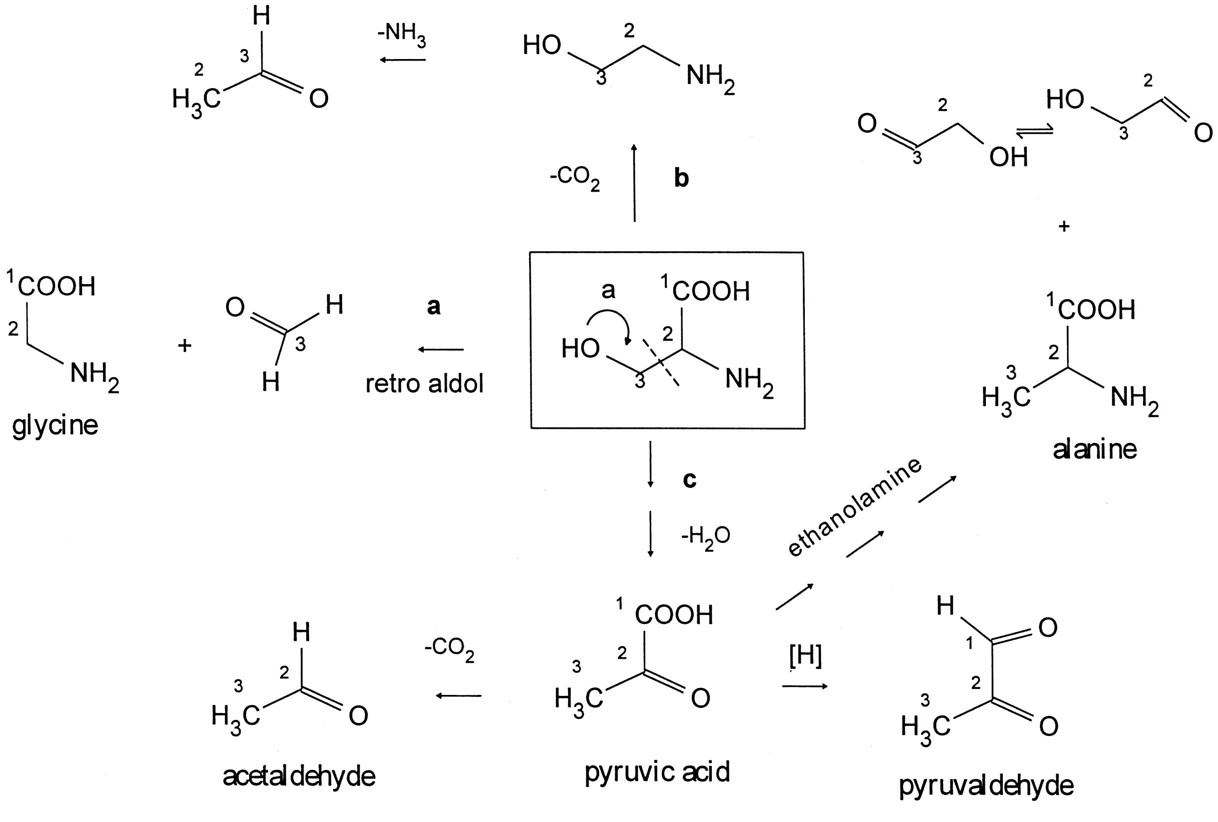

Fig. 1. Initial thermal degradation pathways (a, b and c) of L-serine (for details see Yaylayan et al., 2000).

due to the detection of 2,5-diketo-3,6-dimethylpiperazine (cyclic alanine dimer) and cycloglycylalanine. The formation of most of the advanced decomposition products of L-serine was rationalized, based on these initial degradation products and by label incorporation studies. For example, the origin of glycolaldehyde and alanine was attributed to the interaction of ethanolamine with pyruvic acid, during which the ethanolamine is converted into glycolaldehyde and pyruvic acid into D,L-alanine (Yaylayan et al., 2000). Due to enolization and isomerization, both C-2 and C-3 atoms of L-serine could be incorporated as the carbonyl carbon of glycolaldehyde, as shown in Fig. 1.

Analysis of the thermal degradation products of L-serine indicated that most of the detected pyrazines were methyl or ethyl-substituted, and similar to pyrroles (see Table 1). However, 2-(1-pyrrolyl)-ethanol was the most abundant pyrrole and was the highest peak in the pyrogram. In general, pyrroles could be formed, either by the interaction of 1,4-dicarbonyls with amines, known as the Paal-Knorr synthesis, or by the reaction of β-diketones with α-halocarbonyls in the presence of amines, known as the Hantzsch pyrrole synthesis. On the other hand, the condensation of α-aminocarbonyls with ketones or aldehydes (**1** in Fig. 2) is the most general and widely applicable method of pyrrole formation, known as the Knorr pyrrole synthesis (Acheson, 1976). The presence of the intermediates of the Knorr pyrrole synthesis pathway (aldehydes and α-aminocarbonyls) in the degradation mixture of L-serine, has been confirmed in a previous study (Yaylayan et. al., 2000). This study also confirmed the importance of the same intermediates as the precursors of pyrazines. The similarity of the substituents of both pyrazines and pyrroles detected in the model system, has prompted us to consider the possibility that pyrroles and pyrazines may have the same precursors in the L-serine model system. α-Aminocarbonyls (**2** and **3** in Fig. 2) can produce mono-substituted pyrazines through dimerization with α-aminoacetaldehyde followed by oxidation, and at the same time can generate pyrroles through aldol condensation (Knorr synthesis) with acetaldehyde (**1**; see Fig. 2). According to this scheme, α-aminoketones can form 3-substituted pyrroles and α-aminoaldehydes can form 2-substituted pyrroles when they interact with acetaldehyde. As shown in Fig. 1, acetaldehyde can be formed through pathway **b** with the incorporation of the C-3 atom of L-serine as the carbonyl carbon and through pathway **c** with the incorporation of the C-2 atom instead.

Table 1
Selected pyrroles and pyrazines detected in the thermal degradation mixture of L-serine

Pyrroles	Pyrazines
1H-Pyrrole	Pyrazine
2-Methylpyrrole	Methylpyrazine
3-Methylpyrrole	Ethylpyrazine
2-Ethylpyrrole	2-Ethyl-6-methylpyrazine
3-Ethylpyrrole	2-Ethyl-3-methylpyrazine
2-(1-Pyrrolyl)-ethanol	2,6-Diethylpyrazine
	2,3-Dimethyl-5-ethylpyrazine

Table 2
Percent incorporation of ^{13}C-1 atom of L-serine in selected pyrroles and pyrazines[a]

m/z	15a	4a	5a	4b	5b	15b	6a	6b
M	100	95	95	100	100	100	90	100
M + 1	0	5	5	0	0	0	10	0

[a] **15a** pyrrole; **4a** 2-methylpyrrole; **5a** 3-methylpyrrole; **4b** 2-ethylpyrrole; **5b** 3-ethylpyrrole; **15b** 2-(1-pyrrolyl)-ethanol; **6a** methylpyrazine; **6b** ethylpyrazine

3.2. Origin of 2- and 3-substituted pyrroles and mono-substituted pyrazines

The above assertion that similar α-aminocarbonyl intermediates are involved in both pyrrole and pyrazine formation, can be verified by comparison of their ^{13}C-label incorporation patterns. In general, α-aminocarbonyl compounds can be formed either through Strecker reaction of amino acids with α-dicarbonyl compounds or through Amadori rearrangement of α-hydroxycarbonyl compounds with ammonia (Yaylayan et al., 2000). Using ^{13}C-labelled L-serine at different carbon atoms and analyzing the label incorporation into methyl- and ethyl-substituted pyrroles and pyrazines (see Tables 2–4), the origin of such precursors can be predicted (see Fig. 3). For example, methylpyrazine can be used to determine the origin of pyruvaldehyde or an equivalent three-carbon precursor unit. Labelling studies have indicated the incorporation of all three carbon atoms of L-serine in different ratios, into both methylpyrazine and methylpyrroles (see Tables 2–4). Analysis of the labeling data confirmed the existence of three pathways of formation of carbonyl precursors of methylpyrazine. The major pathway (70%) involved aldol addition of formaldehyde to glycolaldehyde to generate glyceraldehyde with two C-3 and one C-2

Table 3
Percent incorporation of ^{13}C-2 atom of L-serine in selected pyrroles and pyrazines[a]

m/z	15a	4a	5a	4b	5b	15b	6a	6b
M	0	0	0	0	0	0	0	0
M + 1	0	0	0	0	0	0	0	0
M + 2	100	60	60	0	0	0	80	0
M + 3	0	40	40	100	100	100	20	100

[a] **15a** pyrrole; **4a** 2-methylpyrrole; **5a** 3-methylpyrrole; **4b** 2-ethylpyrrole; **5b** 3-ethylpyrrole; **15b** 2-(1-pyrrolyl)-ethanol; **6a** methylpyrazine; **6b** ethylpyrazine

atoms of L-serine (see Fig. 4). The subsequent reaction of ammonia with glyceraldehyde can generate the Amadori rearrangement product, 1-amino-3-hydroxyacetone (**7**). Alternatively, glyceraldehyde can be dehydrated into pyruvaldehyde, which in turn can undergo Strecker reaction on either of the carbonyl carbons, to generate both 2-aminopropionaldehyde (**8**) and 1-aminoacetone (**9**), both consisting of two C-3 and one C-2 atoms of L-serine. Only the latter two aminocarbonyls (**8**, **9**) can form both methylpyrroles and methylpyrazine with the indicated distribution of carbon atoms of L-serine, whereas intermediate 7 can form only pyrazines. Label incorporation studies showed that methylpyrroles, consisting of this pattern of L-serine carbon atom incorporation, constituted 55% of the total methylpyrrole distribution. Interestingly, 2- and 3-subsituted pyrroles had identical label incorporation patterns which further supports the mechanism shown in Fig. 4. Pyruvaldehyde, generated from the reduction of pyruvic acid (see Fig. 1), can similarly undergo Strecker reactions to form both 2-aminopropionaldehyde (**8**) and 1-aminoacetone (**9**), this time incorporating one C-1, one C-2 and one C-3 atoms of L-serine. This pathway constituted 10% of the total methylpyrazine and 5% of total methylpyrrole formations. The third pathway (see Fig. 5) involves the interaction of glycine with glycolaldehyde (Yaylayan et al., 2000) to eventually form 1-aminoacetone (**13a**) and 2-aminopropionaldehyde (**12a**) incorporating two C-2 and one C-3 atoms of L-serine. This pathway constituted 20% of the total methylpyrazine and 40% of total methylpyrrole formation. The existence of an additional pathway

Table 4
Percent incorporation of ^{13}C-3 atom of L-serine in selected pyrroles and pyrazines[a]

m/z	15a	4a	5a	4b	5b	15b	6a	6b
M	0	0	0	0	0	0	0	0
M+1	0	0	0	0	0	0	0	0
M+2	100	40	40	0	0	0	30	0
M+3	0	60	60	100	100	100	70	100

[a] **15a** pyrrole; **4a** 2-methylpyrrole; **5a** 3-methylpyrrole; **4b** 2-ethylpyrrole; **5b** 3-ethylpyrrole; **15b** 2-(1-pyrrolyl)-ethanol; **6a** methylpyrazine; **6b** ethylpyrazine

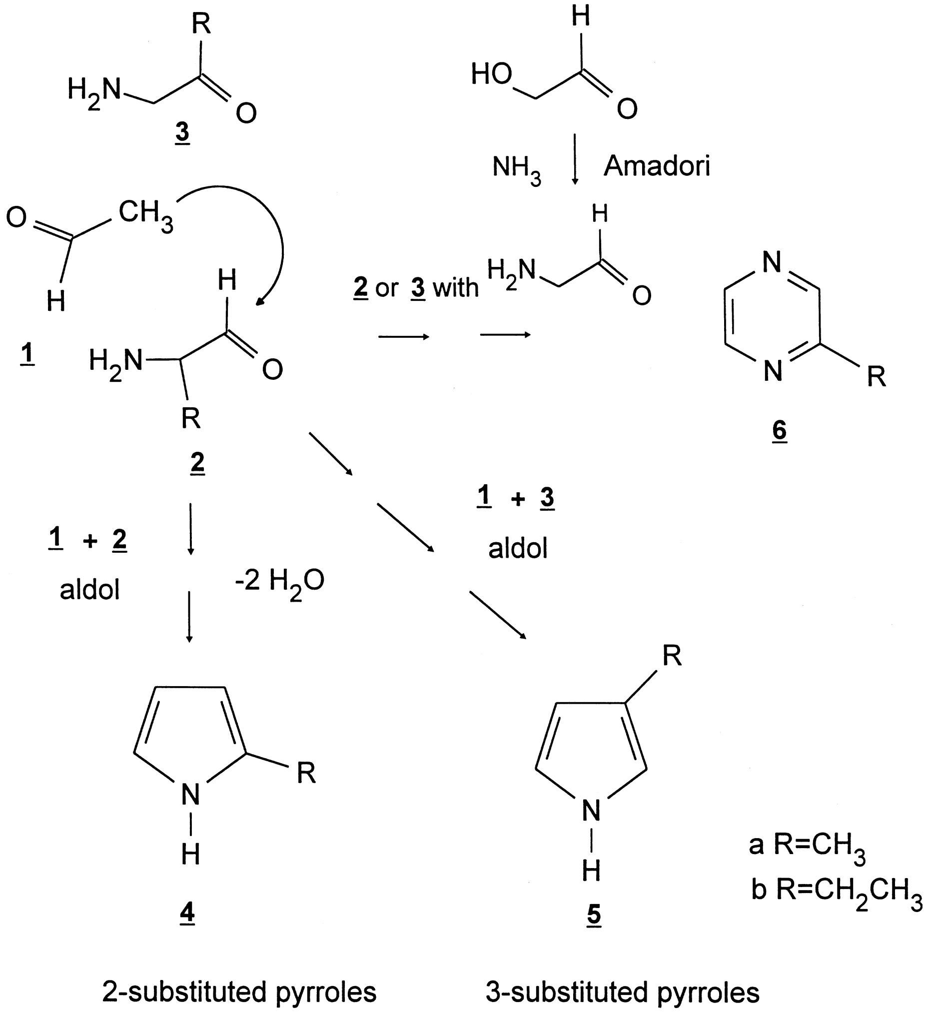

Fig. 2. Proposed mechanism of formation of 2- and 3-substituted pyrroles (**4** and **5**) and mono-substituted pyrazines (**6**).

(through intermediate **7**) leading only to the formation of methylpyrazine, accounts for the differences in the percentage distribution of different pathways between methylpyrroles and methylpyrazine. On the other hand, label incorporation studies have further indicated the existence of only one pathway of formation of ethylpyrazine and ethylpyrroles. According to Fig. 5, replacing glycine with alanine can generate the precursors (**12b**, **13b**) for ethyl-substituted pyrroles and pyrazine with the expected label incorporation pattern (Tables 2–4). All the above α-aminocarbonyls (8, 9, 12 and 13) are able to form pyrazines, with the observed label distribution pattern, by reaction with 2-aminoacetaldehyde (**14a**) and form pyrroles through interaction with acetaldehyde as shown in Fig. 2.

3.3. Origin of 1H-pyrrole and 2-(1-pyrrolyl)-ethanol

According to Fig. 5 the parent pyrrole (**15a**) can be formed by the aldol condensation of aminoacetaldehyde

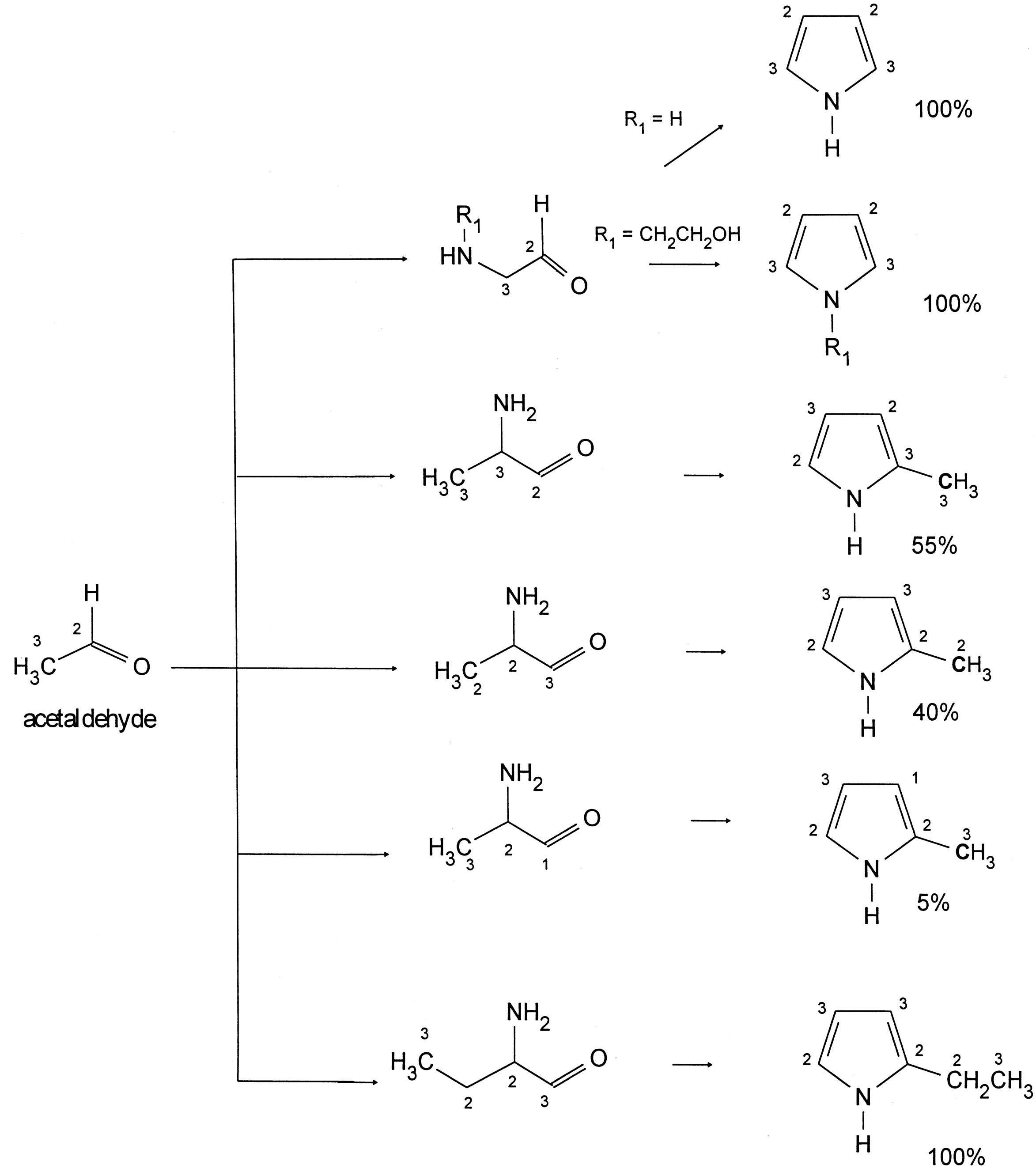

Fig. 3. Carbonyl precursors and percent isotopomers of pyrroles calculated, based on the data in Tables 2–4. The relative positions of C-2 and C-3 atoms originating from glycolaldehyde or acetaldehyde can be interchanged. Numbers indicate original carbon atom positions of L-serine. Mechanism of formation according to Fig. 2.

(**14a**) with acetaldehyde followed by cyclization and loss of water as depicted in Fig. 2 for other pyrroles. Similarly, 2-(1-pyrrolyl)-ethanol can be formed by a similar process starting with **14b**. The Amadori rearrangement reaction of glycolaldehyde with ammonia and ethanolamine can generate **14a** and **14b** respectively. Consequently, both pyrroles should have one pathway of formation with incorporation of two C-2 and two C-3 atoms of L-serine in the case of the parent pyrrole and with incorporation of three C-2 and three C-3 atoms of L-serine in the case of 2-(1-pyrrolyl)-ethanol. Labeling data shown in Tables 2–4 confirm this predication.

3.4. Further confirmation of the proposed pathways

The proposed mechanism shown in Fig. 4 is based on the assumption that the main source of formaldehyde is the pathway **a** in Fig. 1 where the C-3 atom of L-serine is incorporated as the sole formaldehyde carbonyl carbon. This assumption can be justified, based on the limited amount of glycine produced from L-serine degradation, thus preventing an extensive Strecker reaction from occurring to produce a significant amount of formaldehyde (incorporating the C-2 atom of L-serine) from glycine. Furthermore, the ability of glycine to undergo double addition rather than Strecker reaction with α-dicarbonyl compounds has been demonstrated (Keyhani & Yaylayan, 1996). However, to confirm the participation of glycine in the formation of precursors of pyrroles, as depicted in Fig. 5, L-serine was pyrolyzed in the presence of excess [^{13}C-2]glycine. The presence of excess [^{13}C-2]glycine in the mixture can also lead to the formation of formaldehyde from glycine as Strecker aldehyde (incorporating the labelled C-2 atom from glycine) and can consequently generate, according to Schemes 3 and 4, unlabeled and singly labelled methylpyrroles. Unlabelled and singly labeled methylpyrroles can be produced through pathway shown in Fig. 4, depending on the source of formaldehyde and only singly labelled methylpyrazine can be formed through the mechanism shown in Fig. 5. Inspection of Table 5 shows data consistent with the above predictions. The higher percentage of singly labelled product (70%) was attributed to the existence of two pathways for its generation. Similar effects (Yaylayan et al., 2000) were also observed in the case of methylpyrazine (see Table 5). On the other hand, ethyl-substituted pyrroles are produced by only one pathway (Fig. 5), through the reaction of alanine with glycolaldehyde to produce 2-aminobutanaldehyde (**12b**) and 1-amino-2-butanone (**13b**). The

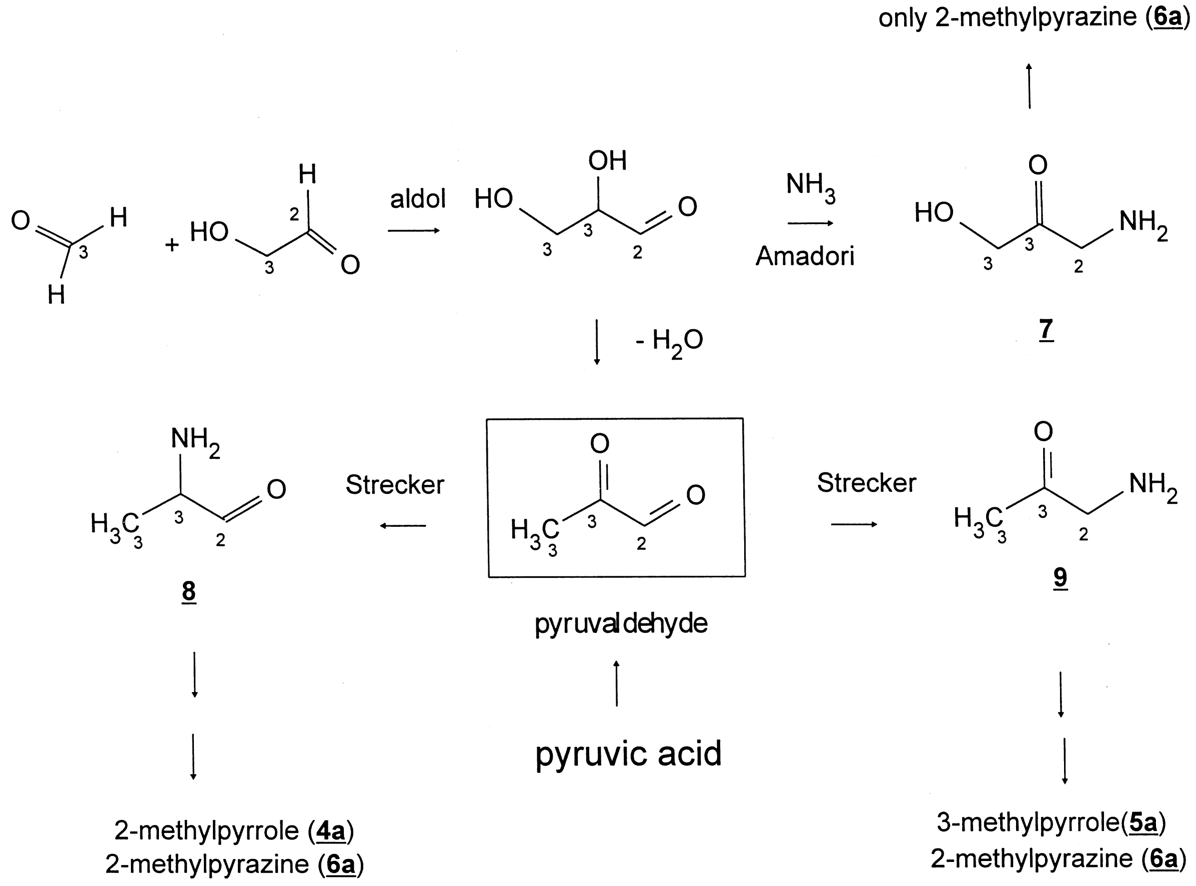

Fig. 4. Proposed pathways of formation of glyceraldehyde and pyruvaldehyde. Numbers indicate original carbon atom positions of L-serine.

aldol condensation of these intermediates with acetaldehyde (Fig. 2) produces ethyl-substituted pyrroles. Acetaldehyde however, is also the Strecker aldehyde of L-alanine. To confirm the participation of alanine in the formation of ethyl-substituted pyrroles and pyrazines, L-serine was also pyrolyzed in the presence of L-[^{13}C-2]alanine. L-Alanine is known to efficiently produce acetaldehyde in the presence of dicarbonyls. Consequently, based on the mechanisms shown in Schemes 1, 2 and 4, the pyrolysis of L-serine in the presence of L-[^{13}C-2]alanine should produce completely unlabelled ethylpyrrole through involvement of alanine and acetaldehyde formed in situ from unlabelled L-serine; it should also produce singly labelled ethylpyrrole through involvement of either added labelled alanine or acetaldehyde produced from it, and finally, it should also generate doubly labelled ethylpyrrole when added labelled alanine and acetaldehyde produced from it, are both involved in the formation of ethylpyrrole, according to Fig. 5. Again, the data presented in Table 5 confirm the above predictions. Similar consistent results were also observed in the case of ethylpyrazine (Table 5). Furthermore, electron impact fragmentation patterns of ethylpyrroles (see Fig. 6) could be used to confirm the identity of the carbon atom of the ethyl group, directly attached to the pyrrole ring. According to the mechanism proposed in Fig. 5, the only carbon atom that could be directly connected to the pyrrole ring is the C-2 atom of L-serine (or C-2 atom of alanine). However, if

Table 5
Percent incorporation of ^{13}C-2 labelled carbon atoms of glycine in methyl- substituted pyrroles/pyrazines and ^{13}C-2 labelled carbon atoms of D,L-alanine in ethyl- substituted pyrroles/pyrazines

	M	M +1	M+2
2- or 3-ethylpyrrole			
L-serine/D,L-[2-^{13}C]alanine (1:3)	40	45	15
Ethylpyrazine			
L-serine/ D,L-[2-^{13}C]alanine (1:3)	40	55	5
2- or 3-methylpyrrole			
L-serine/[2-^{13}C]glycine (1:3)	30	70	0
Methylpyrazine			
L-serine/[2-^{13}C]glycine (1:3)	25	75	0

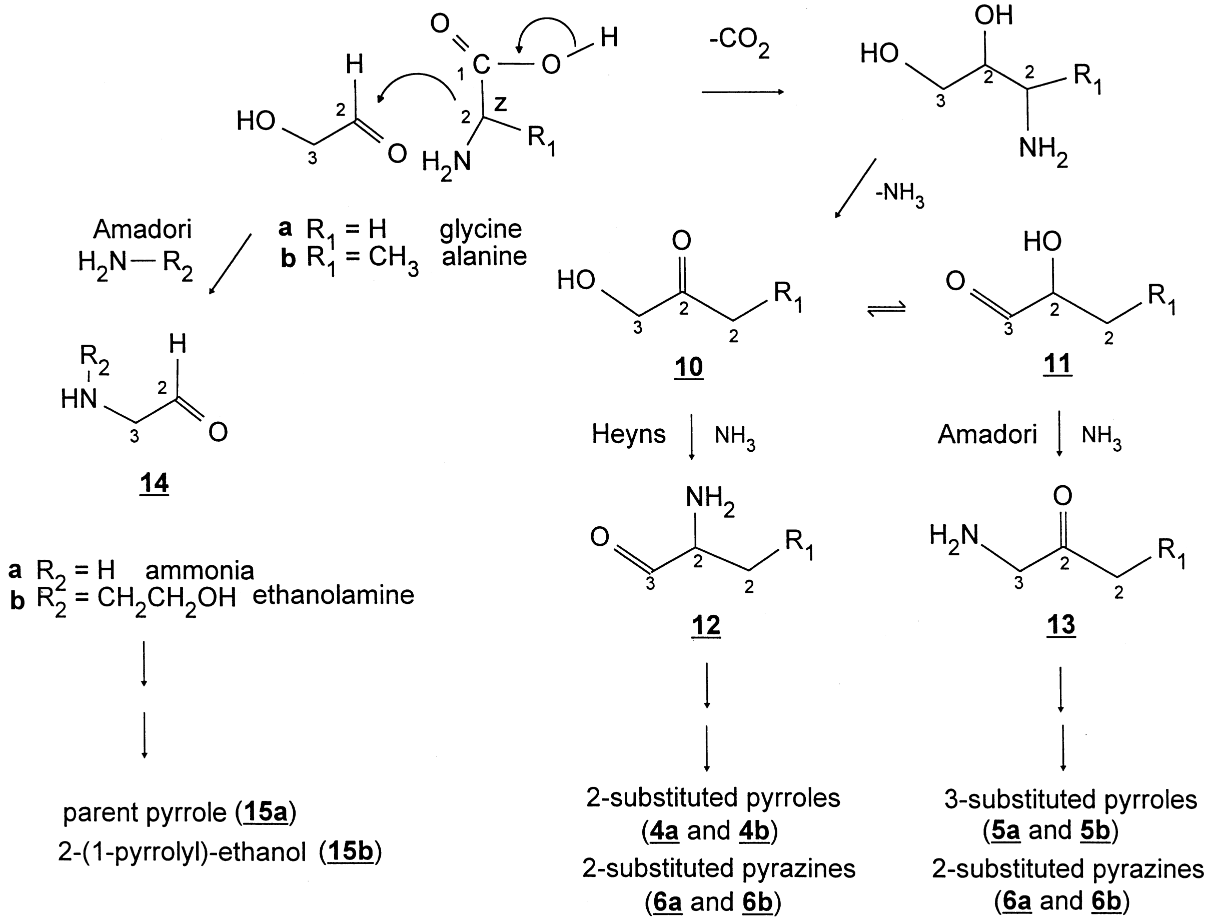

Fig. 5. Proposed pathways of formation of 1-hydroxyacetone (**10a**), 1-hydroxy-2-butanone (**10b**), 2-hydroxypropionaldehyde (**11a**) and 2-hydroxybutanaldehyde (**11b**). Numbers indicate original carbon atom positions of L-serine.

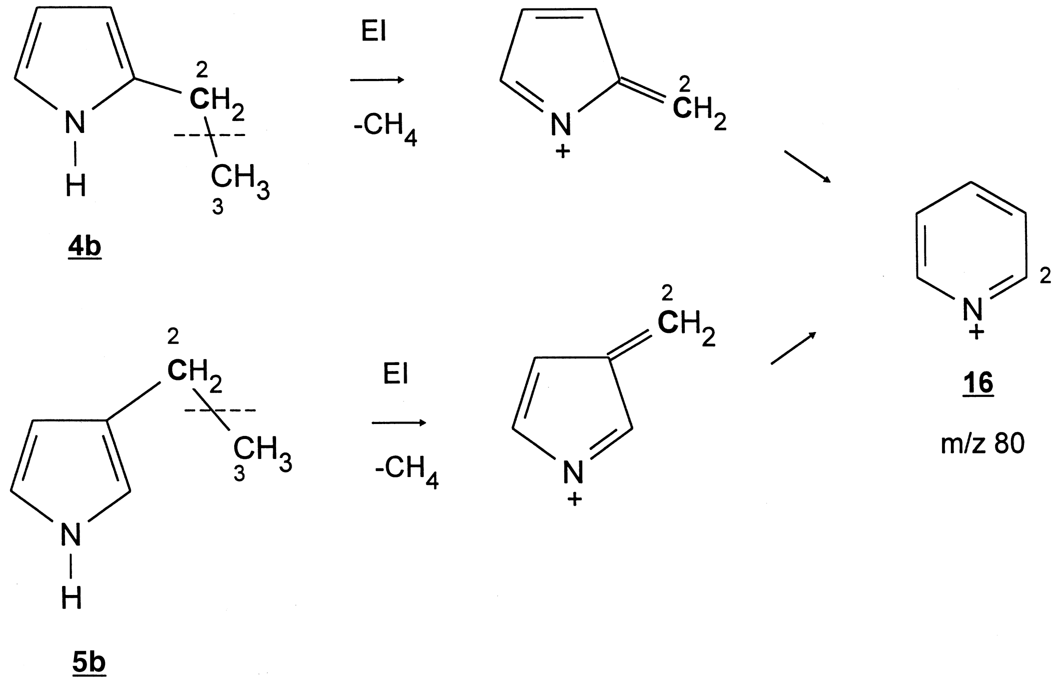

Fig. 6. Formation of pyridinium ion (**16**) at **m/z** 80 from electron impact fragmentation of ethylpyrroles. Numbers indicate original carbon atom positions of L-serine.

Table 6
Percent incorporation of ^{13}C-labeled atoms of L-serine in pyridinium ion (**16**) formed under EI fragmentation of 2- or 3-ethylpyrroles

m/z	L-serine	L-[^{13}C-1]serine	L-[^{13}C-2]serine	L-serine[a]	L-[^{13}C-3]serine
80	100	100	0	65	0
81	0	0	0	30	0
82	0	0	0	5	100
83	0	0	100	0	0

[a] Mixed with D,L-[^{13}C-2]alanine.

through a different mechanism, the ethyl group originated either from acetaldehyde or glycolaldehyde, then the carbon atom directly attached to the pyrrole ring should have a mixed origin (C-2 and C-3), since the positions of these atoms in acetaldehyde or glycolaldehyde are not fixed (see Fig. 1). During electron impact fragmentation, 2- or 3-ethylpyrroles lose a neutral methane molecule to produce the pyridinium ion (**16**) at **m/z** 80 (see Fig. 6). According to Fig. 3, ethyl-pyrrole incorporates three C-3 and three C-2 atoms of L-serine; consequently, the pyridinium ion (**16**) of ethylpyrrole generated from L-[^{13}C-3]serine, should incorporate only two C-3 atoms. However, the same ion, generated from L-[^{13}C-2]serine, should incorporate all the three C-2 atoms if the mechanism shown in Fig. 5 is correct. Inspection of Table 6 indicates that the data are consistent with the above predictions and that the loss of a methane molecule involved only C-3 atoms, indicating that the direct link to the pyrrole ring is only through C-2 atoms.

4. Conclusion

Degradation of L-serine in the absence of sugars can lead to the formation of different α-aminocarbonyl intermediates that are the common precursors to pyrazines and pyrroles.

Acknowledgements

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

References

Acheson, R. M. (1976). *An introduction to the chemistry of heterocyclic compounds* (3rd ed.). New York: John Wiley.

Baltes, W., & Bochmann, G. (1987). Model reactions on roast aroma formation. 1. Reaction of serine and threonine with sucrose under the conditions of coffee roasting and identification of new coffee aroma compounds. *Journal of Agriculture and Food Chemistry, 35*, 340–346.

Kato, S., Kurata, T., Ishitsuka, R., & Fujimaki, M. (1970). Pyrolysis of β-hydroxy amino acids, especially L-serine. *Agriculture Biology and Chemistry, 34*, 1826–1832.

Keyhani, A., & Yaylayan, V. (1996). Elucidation of the mechanism of pyrazinone formation in glycine model systems using labeled sugars and amino acid. *Journal of Agriculture and Food Chemistry, 44*, 2511–2516.

Reese, G., & Baltes, W. (1993). Model reactions on roast aroma formation. XI. (1992). Heating of serine with selected sugars and sugar degradation products in an autoclave. *Z. Lebensm. Unters Forsch., 194*, 417–421.

Wang, P-S., & Odell, G. V. (1973). Formation of pyrazines from thermal treatment of some amino-hydroxy compounds. *Journal of Agriculture and Food Chemistry, 21*, 868–870.

Yaylayan, V., & Keyhani, A. (1998). The origin and fate of α-dicarbonyls formed in Maillard model systems: mechanistic studies using ^{13}C- and ^{15}N-labeled amino acids. In J. O'Brien, H. E. Nursten, M. J. Crabbe, & J. Ames, *The Maillard reaction in foods and medicine* (pp. 51–56). Cambridge, UK: Royal Society of Chemistry.

Yaylayan, V., Keyhani, A., & Huyghues-Despointe, A. (1998). Generation and the fate of C_2, C_3, and C_4 reactive fragments formed in Maillard model systems of [^{13}C]glucose and [^{13}C]glycine or proline. In F. Shahidi, C-T. Ho, & C. Van Nguyan, *Process induced chemical changes in food* (pp. 237–244). New York: Plenum Press.

Yaylayan, V., Keyhani, A., & Wnorowski, A. (2000). Formation of sugar-specific reactive intermediates from ^{13}C-labeled L-serines. *Journal of Agriculture and Food Chemistry, 48*, 636–641.