Degradation Products Formed from Glucosamine in Water

Chi-Kuen Shu

Bowman Gray Technical Center, R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina 27105

An aqueous solution of glucosamine hydrochloride was heated to 150 °C for 5 min under different pH conditions. The reaction product mixture obtained was analyzed by GC/MS. It was found that the major products formed were furfurals, especially at pH = 4 and 7. At pH = 8.5, additional flavor components were generated, including pyrazines, 3-hydroxypyridines, pyrrole-2-carboxaldehyde, furans, acetol, and several other compounds. Of the components identified, it is worthwhile to note the formation of pyrazine and methylpyrazine as major components at pH = 8.5. It is proposed that a retro-aldol condensation plays an important role in the formation of the intermediates, α-aminoacetaldehyde (I) and α-amino propanal (II). As a result, self-condensation of I generates pyrazine and combination of I and II generates methylpyrazine. In addition, it is also interesting to note the formation of 3-hydroxypyridines and pyrrole-2-carboxaldehyde. It is suggested that both groups of compounds are derived from furfurals. As the ammonia is liberated from glucosamine, it initiates the ring-opening of furfurals to form 5-amino-2-keto-3-pentenals. Intramolecular condensations of these intermediates between the amino group and the carbonyl groups lead to the formation of 3-hydroxypyridines and pyrrole-2-carboxaldehyde.

Keywords: *Glucosamine; retro-aldol condensation;* α*-amino acetaldehyde;* α*-amino propanal; GC/MS*

INTRODUCTION

It is well-known that the first step of the amino acid-reducing sugar reaction is a sugar amine condensation, leading to an N-substituted Amadori or Heyns intermediate, from which the flavor compounds are generated via subsequent rearrangements and/or degradation reactions. Similarly, when the amino acid is replaced with ammonia, the sugar amine condensation also occurs, initially forming the simple sugar amine instead of an Amadori or Heyns intermediate. Previous studies on the flavor formation from Amadori and Heyns compounds are abundant (Vernin and Parkanyi, 1982; Finot et al., 1990; Labuza et al., 1994), but the information on flavor formation from simple sugar amines is limited. The objective of this study was to identify the degradation products formed from glucosamine in water at different pH values and to propose the formation mechanism of some of the products identified.

EXPERIMENTAL PROCEDURES

Materials. Glucosamine hydrochloride, sodium hydroxide, anhydrous sodium sulfate, furfural, and diammonium hydrogen phosphate were purchased from Aldrich Chemical Co. (Milwaukee, WI). A DB-Wax fused silica column was purchased from J&W Scientific, Inc. (Folsom, CA).

Preparation of the Reaction Mixtures. In an enclosed reaction vessel (Parr Instrument Co., Moline, IL), each solution of glucosamine hydrochloride (5 g) and water (70 mL) was heated at 150 °C for 5 min under different pH conditions (4, 7, and 8.5). The pH of the original solution was 4, while that of the other two solutions was adjusted to 7 and 8.5 by adding 5% NaOH. Each reaction mixture obtained was adjusted to pH 7 with NaOH and extracted with ethyl acetate (50 mL × 3). The combined extracts were dried over anhydrous Na_2SO_4 and concentrated by a rotary evaporator to 25 mL prior to the GC/MS analysis.

Reaction of Furfural and Diammonium Hydrogen Phosphate. Under the above conditions, the reaction of furfural (1 g), diammonium hydrogen phosphate (2 g), and water (70 mL) was performed.

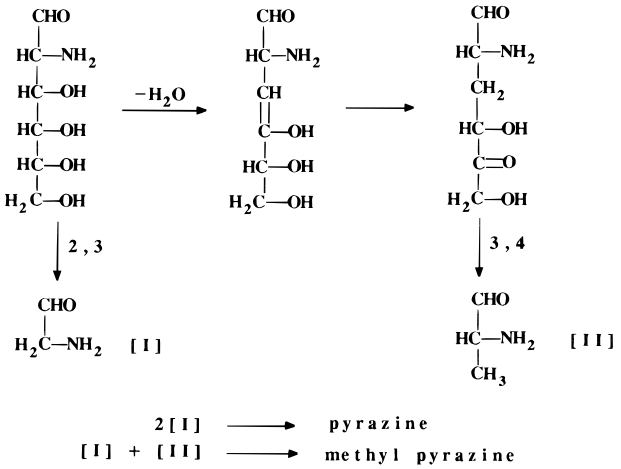

Figure 1. Mechanism proposed for the formation of pyrazine and methylpyrazine.

GC/MS Analysis. The concentrated extracts were analyzed by GC/MS on a DB−Wax fused silica column (30 m × 0.32 mm, 0.15 μm film thickness) with splitless injection. The oven temperature was programmed from 50 to 200 °C at 3 °C/min; a mass selective detector (EI; 70 eV) was used. The NBS library was used for MS search.

Quantitative Estimate. The internal standard, ethyl undecanoate, was added to each concentrated extract, which was then analyzed under the same chromatographic conditions except a flame ionization detector was used. The response factor of the internal standard was used for those of the mixture components. The quantitative results obtained were reported as parts per million (ppm) parts of glucosamine used.

RESULTS AND DISCUSSION

The components identified from the three glucosamine reaction mixtures along with the quantitative data were

S0021-8561(97)00812-1 CCC: $15.00
Published on Web 02/12/1998

Table 1. Components Identified from the Reactions Heated at 150 °C for 5 min and the Quantities Estimated (ppm)

component identified	pH = 4	pH = 7	pH = 8.5	component identified	pH = 4	pH = 7	pH = 8.5
pyrazine	trace	trace	371	furan-2,5-dicarboxaldehyde	17	22	
methylpyrazine			517	quinaxoline			11
acetoin			trace	2-(2-furyl)pyrazine			16
acetol			97	2-(hydroxyacetyl)furan	trace	12	trace
2,6-dimethylpyrazine			11	pyrrole-2-carboxaldehyde	16	9	166
ethylpyrazine			30	2-(hydroxyethyl)pyrazine			181
2,3-dimethylpyrazine			21	3-hydroxy-4,5-dihydro-2(3*H*)-furanone		trace	127
vinylpyrazine			132				
acetic acid			18	hydroxymaltol[a]			30
furfural	46	123	72	3-hydroxy-2-methylpyridine			trace
2-acetylfuran			25	3-hydroxy-6-methylpyridine			trace
1-hydroxy-3-butanone			trace	3-hydroxypyridine	trace	trace	180
5-methylfurfural	trace	trace	trace	(hydroxymethyl)pyridine isomer			141
2-acetylpyrazine			trace	5-(hydroxymethyl)furfural	2283	460	488
furfuryl alcohol			187	2-acetyl-5-(hydroxymethyl)furan			240
cyclotene		trace	trace				

[a] 2,3-Dihydro-3,5-dihydroxy-6-methylpyran-4-one.

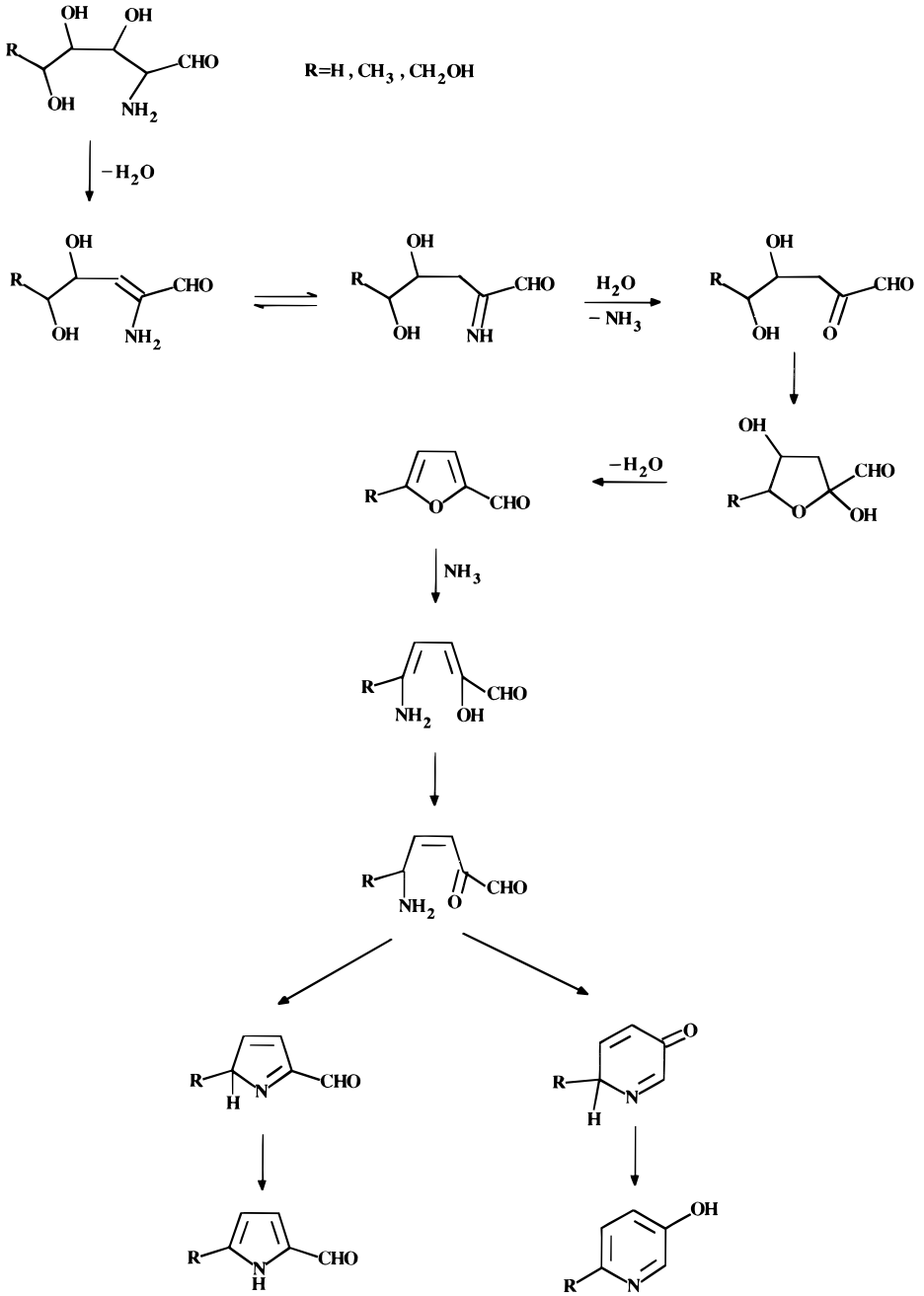

Figure 2. Mechanism proposed for the formation of 3-hydroxypyridines and pyrrole-2-carboxaldehydes.

compiled in Table 1. These results revealed that the major products formed from the thermal degradation of glucosamine in water were furfurals, especially at pH = 4 or 7. At pH = 8.5, additional flavor components were generated, which included pyrazines (pyrazine and methylpyrazine were the major components), 3-hydroxypyridines, pyrrole-2-carboxaldehyde, furans, hydroxy ketones, and several other compounds.

Of the components identified, it is worthwhile to note the formation of the unsubstituted pyrazine, methylpyrazine, 3-hydroxypyridines, and pyrrole-2-carboxaldehyde. For the formation of these two major pyrazines, these data suggest that a retro-aldol condensation plays an important role in the formation of the intermediates, α-aminoacetaldehyde (I) and α-amino propanal (II). As a result, self-condensation of I generates pyrazine and combination of I and II generates methylpyrazine (Figure 1). It is also proposed that both groups, 3-hydroxypyridines and pyrrole-2-carboxaldehyde may be derived from furfurals. Mechanistically, the ammonia, liberated from glucosamine, initiates the ring-opening of furfurals to form 5-amino-2-keto-3-pentenals, as shown in Figure 2. Intramolecular condensation of these intermediates between the amino group and the aldehyde group leads to the formation of 3-hydroxypyridines, while a similar condensation between the amino group and the keto group leads to the formation of pyrrole-2-carboxaldehydes. To support the proposed mechanism, the reaction of furfural and diammonium hydrogen phosphate (used as an ammonia source) was performed under similar conditions. As expected, both 3-hydroxypyridine and pyrrole-2-carboxaldehyde were generated as the major components, providing further substantiation for the proposed formation mechanism.

LITERATURE CITED

Finot, P. A., Aeschbacher, H. U., Hurrell, R. F., Liardon, R., Eds. *The Maillard Reaction in Food Processing, Human Nutrition and Physiology*; Birkhauser Verlag: Basel, Switzerland, 1990.

Labuza, T. P., Reineccius, G. A., Monnier, V. M., O'Brien, J., Baynes, J. W., Eds. *Maillard Reactions in Chemistry, Food, and Health*; The Royal Society of Chemistry: Cambridge, England, 1994.

Vernin, G.; Parkanyi, C. Mechanisms of formation of heterocyclic compounds in Maillard and pyrolysis reactions. In *The Chemistry of Heterocyclic Flavouring and Aroma Compounds*; Vernin, G., Ed.; Ellis Horwood: Chichester, U.K., 1982, pp 151−207.

Received for review September 18, 1997. Revised manuscript received December 15, 1997. Accepted December 17, 1997.

JF970812N