Some Volatile Compounds Formed from Thermal Interaction of Glucose with Glycine, Diglycine, Triglycine, and Tetraglycine

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Equimolar aqueous solutions of glycine, diglycine, triglycine, and tetraglycine were heated separately with D-glucose at 180 °C at pH 4–5 in a Parr bomb for 2 h. The volatile compounds generated from the reaction were analyzed by gas chromatography and gas chromatography–mass spectrometry. The Maillard reaction of glucose with glycine and triglycine produced significantly greater amounts of pyrazines than that with either diglycine or tetraglycine. The similarity of the results of glycine with triglycine and diglycine with tetraglycine in the pyrazine formation also suggests that tripeptides or tetrapeptides could be degraded through diketopiperazines.

INTRODUCTION

The Maillard reaction is a well-known reaction that occurs in food during cooking. Because of the complexities of the Maillard reaction, many investigations have been aimed at understanding the mechanisms of the reaction. The pathways for the Maillard reaction originally proposed by Hodge (1953) have gained wide acceptance.

Recent works on the generation of aroma compounds from the Maillard reaction were mostly concerned with simple model systems using amino acids. Some of the amino acids used in model systems were proline (Shigematsu et al., 1975; Tressl et al., 1985a–c), hydroxyproline (Tressl et al., 1985d), serine and threonine (Baltes and Bochmann, 1987), cysteine (Shu and Ho, 1988; Zhang and Ho, 1991), leucine (Hartman et al., 1984), and glycine (Olsson et al., 1971; Hayashe et al., 1985).

Although a wide range of peptides has been reported in considerable quantity in many food systems such as aged sake (Takahashi et al., 1974), meat (Mabrouk, 1976), and hydrolyzed vegetable protein (Manley et al., 1981), the role of peptides as precursors in the generation of flavor compounds has not been investigated to an appreciable extent. Chuyen et al. (1973) studied the reaction of various dipeptides with glyoxal and reported the identification of 2-(3′-alkyl-2′-oxopyrazin-1′-yl)alkyl acids as major products. Most recently, Rizzi (1989) reported that model Maillard reactions of dipeptides and tripeptides with fructose generated Strecker degradation products, such as Strecker aldehydes and alkylpyrazines, from amino acids with blocked amino and carboxyl functionalities.

This paper reports the reactivity of glycine and its simple peptides toward glucose in the generation of volatile flavor compounds.

EXPERIMENTAL PROCEDURES

Sample Preparation. Mono-, di-, tri-, and tetraglycine (Sigma Chemical Co., St. Louis, MO) (0.002 mol each) were separately dissolved with 0.002 mol of D-glucose in 50 mL of distilled water. Each sample mixture was transferred into a 0.3-L Hoke SS-DOT sample cylinder and heated in an oil bath at 180 °C for 2 h. The pH of each reaction mixture was 4.2–4.4. Each reaction mixture was adjusted to pH >12 with NaOH and then extracted with methylene chloride, containing an internal standard, in a separatory funnel by multiple extraction fashion (5 × 50 mL). The methylene chloride extracts were dried over anhydrous sodium sulfate and concentrated by blowing with nitrogen gas to a final volume of 0.2 mL.

Volatile Separation by Gas Chromatography. A Varian 3400 gas chromatograph equipped with an FID and a nonpolar fused silica capillary column [50 m × 0.32 mm (i.d.), 1.05-μm thickness, HP-1; Hewlett-Packard] was used to analyze the volatile compounds isolated from the thermal reaction systems. For each sample, 0.2 μL was injected with a split ratio of 50:1. The GC was run with an injector temperature of 270 °C, a detector temperature of 300 °C, and a helium carrier flow rate of 0.8 mL/min. The temperature program included an initial column temperature of 40 °C, a temperature increase of 2 °C/min from 40 to 260 °C, and a 10-min isothermal period at the final column temperature.

Quantitative determination was accomplished by using *p*-cymene as an internal standard. The quantity of each component was finally converted into milligrams of volatiles generated by 1 mol of glycine or peptides. Linear retention indices for the volatile compounds were calculated by using *n*-paraffin standards (C_6–C_{26}, Alltech Associates) as references (Majlat et al., 1974).

GC–MS Analysis. The concentrated samples were analyzed by GC–MS using a Varian 3400 gas chromatograph coupled to a Finnigan MAT 8230 high-resolution mass spectrometer, using the same GC program as for the separation. Mass spectra were obtained by electron ionization at 70 eV and a source temperature of 250 °C. The filament emission current was 1 mA, and spectra were recorded on a Finnigan MAT SS 300 data system.

RESULTS AND DISCUSSION

Table I lists the volatile compounds generated when an equimolar solution of glycine, diglycine, triglycine, or tetraglycine was reacted with D-glucose at 180 °C for 2 h. From the quantitative data, it was observed that glycine or triglycine generated a larger amount of alkylpyrazines than either diglycine or tetraglycine.

It is also interesting to note that furfural and 5-(hydroxymethyl)furfural were produced in a greater quantity in the reaction of diglycine and tetraglycine with glucose compared to that with glycine or triglycine. Furfurals were formed from the catalytic degradation of glucose by amino compounds via the enol form of 3-deoxy-D-*erythro*-hexosulose which followed by dehydration, oxidation and disproportionation (Olsson et al., 1978). 2-Acetylpyrrole

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Table I. Amount of Volatile Compounds Generated by Glycine, Diglycine, Triglycine, and Tetraglycine with Glucose at 180 °C for 2 h

		mg/mol of amino compd			
compd	I_k[a]	Gly	di-Gly	tri-Gly	tetra-Gly
pyrazine	738	12.18			
methylpyrazine	798	257.80		186.81	3.17
furfural	808	14.14	100.44	3.87	16.93
2,5-dimethylpyrazine	887	360.86	10.28	266.57	46.88
2,6-dimethylpyrazine	894	198.76		139.50	17.41
trimethylpyrazine	980	486.77	8.11	375.98	54.52
2-acetylpyrrole	1058	1.36		1.59	
tetramethylpyrazine	1065	71.44		55.63	
5-(hydroxylmethyl)furfural	1208	125.61	797.04		127.41

[a] Linear retention indices were calculated according to Majlat et al. (1974) on an HP-1 column.

and 2-formyl-5-methylpyrrole were identified as trace components in these model reactions.

The formation of diketopiperazines from the thermal degradation of dried polyglycine has been reported by Hayase et al. (1975). From Table I, the relative abundances of pyrazines formed from glycine and triglycine are very close. However, the amount of pyrazines formed from diglycine or tetraglycine was considerably less as compared to that from either glycine or triglycine. The triglycine could be degraded into glycine and diglycine through diketopiperazine, while tetraglycine was degraded primarily into diglycine, and further degradation of diglycine into glycine could require more energy. On the other hand, the degradation of peptides by direct hydrolysis without the intermediate formation of diketopiperazine cannot be ruled out.

The reactivity order, tetraglycine > triglycine > diglycine > glycine, for color formation in the browning reaction reported by Chuyen et al. (1977) differs from our observation for the pyrazine formation. This clearly indicated that for the Maillard reaction the melanoidin formation is different from aroma formation in mechanism and reactivity.

Peptides that are abundant in foods can serve as unique precursors of processed food aromas.

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Registry No. D-Glucose, 50-99-7; glycine, 56-40-6; diglycine, 556-50-3; triglycine, 556-33-2; tetraglycine, 637-84-3; pyrazine, 290-37-9; methylpyrazine, 109-08-0; furfural, 98-01-1; 2,5-dimethylpyrazine, 123-32-0; 2,6-dimethylpyrazine, 108-50-9; trimethylpyrazine, 14667-55-1; 2-acetylpyrrole, 1072-83-9; tetramethylpyrazine, 1124-11-4; 5-(hydroxylmethyl)furfural, 67-47-0.