

Model System for Cookies: Volatile Components Formed from the Reaction of Sugar and β -Alanine

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The mixture of fructose or glucose with β -alanine was heated in a heater block at 150 °C for 4–8 min. The volatile compounds were extracted with dichloromethane and identified by gas chromatography/mass spectrometry using a fused silica capillary column. In the reaction of fructose and β -alanine, 11 heterocyclic compounds, viz., 4 furans, 3 pyrans, and 4 pyrroles, were detected. These compounds were the same as the compounds produced in the reaction of glucose and β -alanine. The major volatile component in the reaction of either fructose or glucose with β -alanine was 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (DDMP). DDMP formation was particularly enhanced using fructose. Maltol, which is known as a component of cookie flavor, is barely detected in either reaction.

INTRODUCTION

Maillard (1912) proposed the browning reaction occurred via the reaction of a carbonyl group of a sugar and an amino group of an amino acid. Hodge (1953) reported that nonenzymatic browning reactions could be demonstrated by using simple model systems instead of actual food systems. Subsequently, many researchers have used simple systems such as a sugar–amino acid mixture to investigate the formation of browning and flavor. Generally, α -alanine (Shigematsu et al., 1972), β -alanine (Hayase and Kato, 1981), glycine (Namiki and Hayashi, 1975; Wu et al., 1985), and proline (Parliment, 1992; Tressl et al., 1985) have been used as a means for supplying an amino group. In most cases, glucose has been used to provide a carbonyl group. Most reactions were conducted in aqueous solution.

In this paper, the volatile products from the reaction of a dry system consisting of fructose or glucose with added β -alanine were investigated. Analysis and identification of the volatile compounds were made by GC, GC/MS, and Kovats indices.

MATERIALS AND METHODS

Materials and Reagents. D-Fructose and β -alanine were high-grade commercial materials. All of the reagents, including 14 hydrocarbons of C₇–C₂₀, were purchased from Sigma Chemical Co. (St. Louis, MO), Phillips Petroleum Co. (Bartlesville, OK), and Aldrich Chemical Co. (Milwaukee, WI).

Sample Preparation. As a model system of baking cookies, the reaction mixtures consisted of equimolar amounts of the sugar (either fructose or glucose, 180 mg) and β -alanine (89 mg). The components were placed in test tubes and the mixtures heated in a heater block at 150 °C for 4–8 min. On cooling, samples were extracted with dichloromethane, and the extract was concentrated to 100 μ L under a nitrogen stream.

Capillary Gas Chromatography (GC)/Mass Spectrometry (MS). A Hewlett-Packard 5792 gas chromatograph coupled with a VG Analytical ZAB-HS-2F mass spectrometer with a VG 11/250 data system was used for mass spectral identification of components. Operating conditions: ionizing voltage, 70 eV; source temperature, 250 °C; accelerating voltage, 8000 eV; filament trap current, 100 mA. The gas chromatograph was modified for use with capillary columns. A 30 m \times 0.25 mm (film

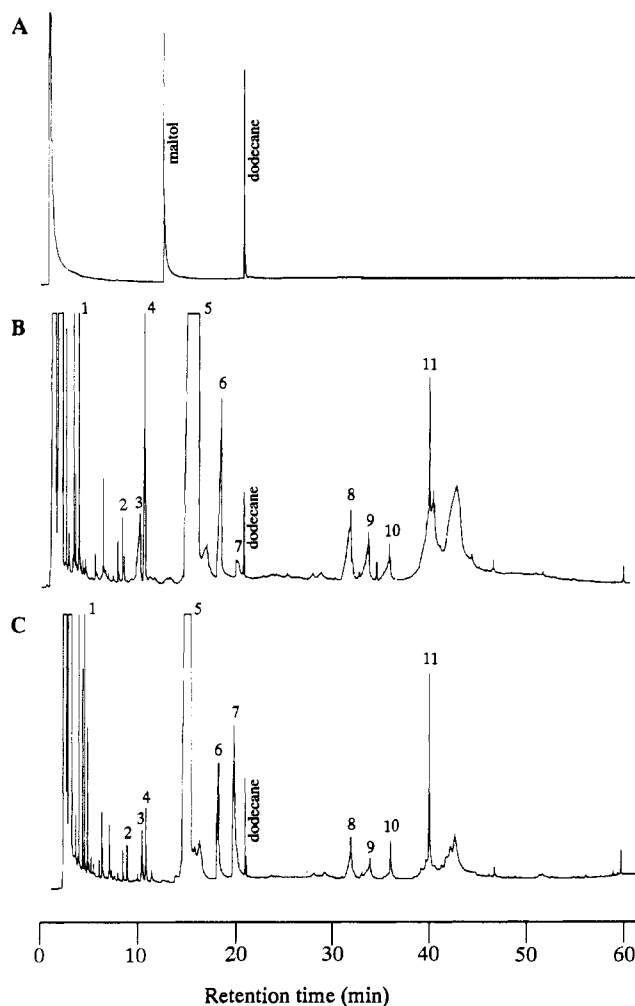


Figure 1. Gas chromatogram of authentic sample and model system extract: (A) maltol; (B) extracts from the reaction of fructose and β -alanine; (C) extracts from the reaction of glucose and β -alanine. GC column: 30 m \times 0.25 mm (i.d.) fused silica capillary column bonded and cross-linked with DB-1 (film thickness 0.25 μ m); temperature program, 50 °C for 8 min, 50–250 °C at 4 °C/min, isothermal hold at 250 °C. Internal standard is dodecane.

thickness, 0.25 μ m) fused silica capillary column bonded and cross-linked with DB-1 was temperature programmed as follows: 50 °C for 8 min, 50–250 °C at 4 °C/min, isothermal hold at 250 °C. Carrier gas velocity was 30 cm/s of He.

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Table I. Compounds of the Volatile Flavor Identified in the Reaction of Fructose and β -Alanine

product	peak no.	Kovats index (DB-1)	mass spectra data, M^+ m/e , or ref
furans			
2-(hydroxymethyl)furan	1	865	98, Parliment (1992)
2-acetyl-3-hydroxy-4,5-dihydrofuran (isomaltol)	2	995	126
furanones			
2,5-dimethyl-4-hydroxy-3(2 <i>H</i>)-furanone	3	1030	128, Parliment (1992)
4-hydroxy-2-acetyl-3(2 <i>H</i>)-furanone	7	1093	142
pyrans			
2,3-dihydro-3-hydroxy-6-methyl-4(<i>H</i>)-pyran-4-one	4	1036	126, Parliment (1992)
2,3-dihydro-3,5-dihydroxy-6-methyl-4(<i>H</i>)-pyran-4-one (DDMP)	5	1123	144, Parliment (1992)
2,3-dihydro-3-hydroxy-6-formyl-4(<i>H</i>)-pyran-4-one	6	1165	142, Parliment (1992)
pyrroles			
3-[<i>N</i> -(2-formylpyrrolyl)]propionic acid	8	1450	167
3-[<i>N</i> -(2-acetylpyrrolyl)]propionic acid	9	1508	181
3-[<i>N</i> -(2-formyl-5-methylpyrrolyl)]propionic acid	10	1568	181
3-[<i>N</i> -(2-formyl-5-(hydroxymethyl)pyrrolyl)]propionic acid	11	1700	197

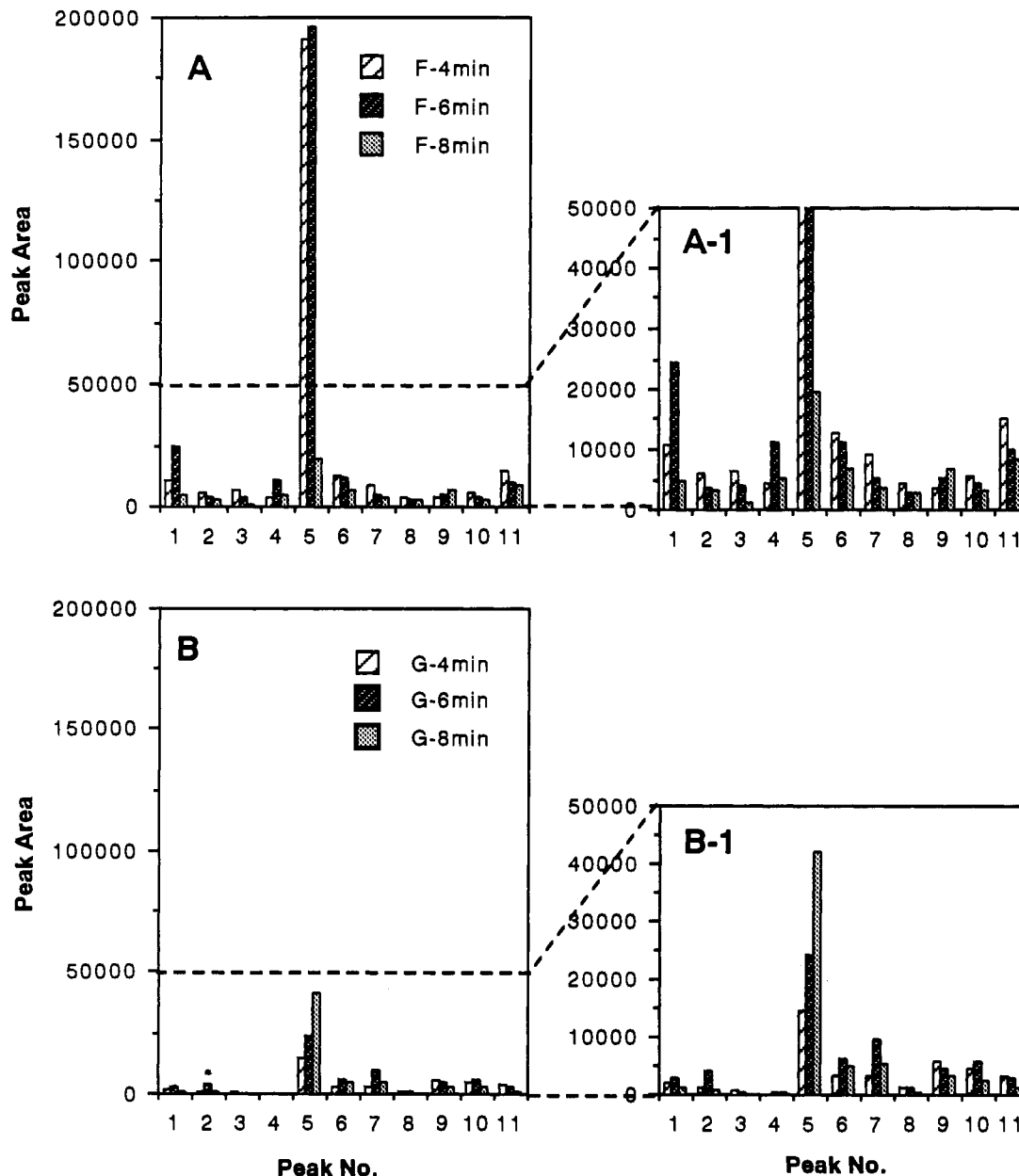


Figure 2. Volatile compounds from the reaction of fructose or glucose with β -alanine: (A) extracts from the reaction of fructose and β -alanine; (B) extracts from the reaction of glucose and β -alanine.

RESULTS AND DISCUSSION

Identification of the Compounds in the Reaction of Reducing Sugar and β -Alanine. Equimolar amounts of fructose and β -alanine were heated in a heater block at 150 °C for 4 min. The volatile compounds from the

reaction mixtures were extracted with dichloromethane and examined by GC and GC/MS. Four furans, three pyrans, and four pyrroles were identified from this reaction (Table I). The major component was identified as 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one

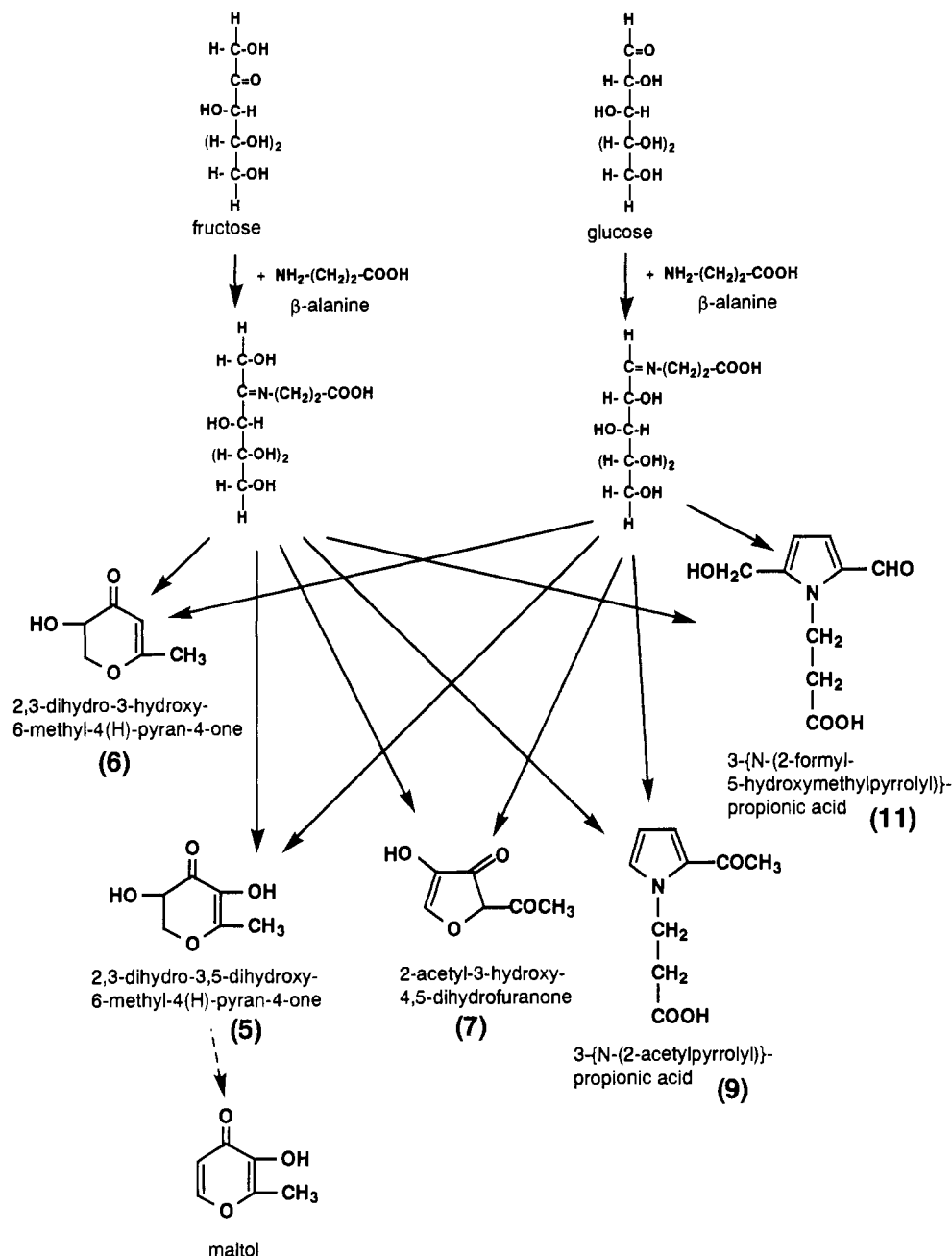


Figure 3. Proposed mechanism of main compounds in the reaction of either fructose or glucose with β -alanine.

(DDMP). Using GC/MS, Parliment (1992) identified DDMP from both reactions of glucose and anhydrous proline heated by microwave and conventional oven. Yaylayan and Mandeville (1991) reported that DDMP was detected in the majority of the Amadori rearrangement products studied by high-resolution EI mass spectrometry. The formation of DDMP was also reported from the reaction of fructose and β -alanine (Nishibori and Bernhard, 1993; Nishibori and Kawakishi, 1991). A large amount of DDMP was formed in cookies using various sugars other than sucrose (Nishibori and Kawakishi, 1990, 1992).

Parliment (1992) detected 2-(hydroxymethyl)furan, 2,5-dimethyl-4-hydroxy-3(2H)-furanone (DHF), 2,3-dihydro-3-hydroxy-6-methyl-4(H)-pyran-4-one, and 2,3-dihydro-3-hydroxy-6-formyl-4(H)-pyran-4-one from the reaction of glucose and anhydrous proline. Mill (1979) also suggested that DHF was formed from an Amadori compound, such as 1-deoxy-1-sarcosino-D-fructose. Yeo and Shibamoto (1991) reported that DHF and DDMP were identified from the reaction of glucose and cysteine with

different moisture contents (0–40%), using microwave irradiation. However, DHF was not detected when only a small amount of water was present. Similar to the system used by Parliment (1992), our systems were also reacted dry without added water. We confirmed DHF was produced in reactions of fructose and glucose with β -alanine. Hodge et al. (1972) described the formation of 2-acetyl-3-hydroxy-4,5-dihydrofuran (isomaltol) from glucose and various amino acids some 20 years ago.

In this investigation, we identified four pyrroles, 3-[N-(2-formylpyrrolyl)]propionic acid, 3-[N-(2-acetylpyrrolyl)]propionic acid, 3-[N-(2-formyl-5-methylpyrrolyl)]propionic acid, and 3-[N-(2-formyl-5-(hydroxymethyl)pyrrolyl)]propionic acid, from the reaction of either fructose or glucose with β -alanine. There are numerous papers concerning the formation of pyrroles from reactions using glucose and various amino acids (Kato, 1967; Kato et al., 1972; Njoroge and Monnier, 1989). These compounds have somewhat similar structures due to the reducing sugars, but there are slight differences between

each compound due to the various amino acids used. In our study, we added β -alanine as the amino acid to sugars for the reaction and then detected pyrroles containing propionic acid.

Confirmation of the Formation of Maltol in the Reaction of either Fructose or Glucose with β -Alanine. Maltol [3-hydroxy-2-methyl-4(*H*)-pyran-4-one] is commonly known as a compound with a sweet aroma and a caramel-like flavor. Maltol is used industrially as a flavor enhancer for improving the quality of food. Patton (1950) reported that maltol was detected when either maltose or lactose was heated with glycine in aqueous solutions. Hodge also described the nonenzymatic formation of maltol from sugars (Hodge and Nelson, 1961) and suggested a reaction mechanism for its formation (Hodge et al., 1972). For many years maltol was mentioned as a principal product of cookie model systems. Recently there has been very little mention of the products (Hiebl et al., 1987; Yeo and Shibamoto, 1991). Little maltol was detected in model systems of baking cookies (Nishibori and Bernhard, 1993; Nishibori and Kawakishi, 1992), and we were unable to confirm the identity of compounds at the position of maltol with a Kovats index of 1065.4 (Table I; Figure 1). Yaylayan and Mandeville (1991) proposed that the formation of maltol is a consequence of electron impact during mass spectrometry of Amadori products and is thus an artifact. They suggest that maltol was formed from DDMP by the ionization of the ring oxygen.

Change of the Amount of Main Compounds Formed in Both Reactions. The mixture 180 mg each of fructose and glucose with 89 mg of β -alanine was heated at 150 °C for 4–8 min. A greater number of volatile compounds was formed from fructose and β -alanine than was formed from glucose and β -alanine (Figures 1 and 2). More DDMP was formed from fructose and β -alanine during the heating periods of 4 and 6 min. The formation, however, decreased when heating time was greater than 8 min. In the case of glucose and β -alanine, the formation of DDMP increased stepwise in proportion to the heating time. This result suggests that the reaction of fructose and β -alanine occurs significantly more rapidly than that of glucose and β -alanine.

The principal compounds formed from fructose or glucose with β -alanine were the same, but the amounts of each compound differed between reactions. Figure 3 shows a proposed mechanism for the formation of the main compounds in both reactions. The formation of compounds 5 (DDMP) and 6, each containing a methyl group, was enhanced using fructose (Figures 1 and 2). On the other hand, compound 7 was a significant component in the reaction of glucose with β -alanine. These results suggest that the reactions of fructose in the Maillard reaction differ from those of glucose. Apparently the reaction of fructose proceeds via the Heyns rearrangement (Heyns and Meinecke, 1953; Heyns and Breuer, 1958) and that of glucose via the Amadori rearrangement.

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