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Food Chemistry 92 (2005) 597–605
Food Chemistry
www.elsevier.com/locate/foodchem

Relative reactivities of glucose and galactose in browning and pyruvaldehyde formation in sugar/glycine model systems

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Received 7 April 2004; received in revised form 31 May 2004; accepted 3 September 2004

Abstract

Glucose/glycine and galactose/glycine model systems were incubated at 45 and 60 °C for the studies of Maillard browning, sugar consumption, and pyruvaldehyde formation. The results showed that, at pH 8, rates of browning followed pseudo-zero-order kinetics. Sugar consumption followed two-staged first-order kinetics with a lower rate constant at the second first-order stage when initial sugar concentration was 2.4% w/v and higher. The yield of pyruvaldehyde followed a third-ordered function of time. Although galactose/glycine system browned at a faster rate, glucose consumed faster than galactose in model systems. The yield of pyruvaldehyde was higher in galactose/glycine systems than in glucose/glycine systems at 45 °C, but inverted at 60 °C.

Keywords: Maillard reaction; Pyruvaldehyde; Glucose; Galactose; Glycine

1. Introduction

Maillard reaction is one of the most important reactions between reducing sugars and amino compounds during food processing and in living bodies (Nishi, Miyakawa, & Kato, 1989). Products of Maillard reaction (MRPs) can be either desirable or undesirable. In addition to brown pigment, some MRPs become flavors or off-flavors in foods (Amrani-Hemaimi, Cerny, & Fay, 1995; Hwang, Hartman, Rosen, Lech, & Ho, 1994; Hwang, Hartman, & Ho, 1995; Keyhani & Yaylayan, 1996; Van Boekel, 1998), some are antioxidative or antimutagenic (Bailey, 1988; Bedinghaus & Ockerman, 1995; Yen, Chau, & Lii, 1993), while others might be potentially toxic to human beings (Kitts, Wu, Stich, & Powrie, 1993; Nursten, 1986; Shibamoto, 1982).

Among these MRPs, pyruvaldehyde, also named as methylglyoxal, has caused much attention of medical scientists because of its potential mutagenecity (Cajelli, Canonero, Martelli, & Brambilla, 1987; Kasai et al., 1982; Shipanova, Glomb, & Nagaraj, 1997; Yim, Kang, Hah, Chock, & Yim, 1995). Fortunately, since puruvaldehyde is a compound of high activity, it reacts readily with other compounds to form volatiles such as butanedione, methylpyrazines, pyrazinones (Chiu, 1994; Keyhani & Yaylayan, 1996; Weenen et al., 1994), and brown pigments (Hayashi & Namiki, 1986). Thus pyruvaldehyde can be beneficial to sensory quality of foods through the formation of flavors and melanoidin, meanwhile reduce its toxicity through consuming pyruvaldehyde itself. Therefore, it is interesting to see how the concentration of pyruvaldehyde varies during food processing and storage. Optimizing the yield of pyruvaldehyde in food would be a challenge to food chemists.

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doi:10.1016/j.foodchem.2004.09.005

In this study, glucose and galactose were used to react with glycine in model systems to study the kinetics of browning rate, sugar consumption, and change of pyruvaldehyde concentration.

2. Materials and methods

2.1. Glucose/glycine model system

Glucose and glycine solutions were prepared by dissolving α-D(+)-glucose (Sigma Chemical Co., USA) and L-glycine (Sigma Chemical Co., USA) in de-ionized water then incubated separately. Concentrations of glucose solution thus prepared were 2.4, 4.8, and 9.6% w/v, respectively, where that of glycine solution was 10.0% w/v. In the beginning of experiments, equal volume of glucose solution and glycine solution at the same temperature were mixed, adjusted pHs to 8.0 using 0.5 N NaOH and 0.5 N HCl solutions, then incubated at 45 °C or 60 °C immediately. Concentrations of glucose and glycine in the mixtures would be half of the original solutions. One hundred and ten milliliter mixture was sampled at intervals for the determination of pH (model SP-71, Suntex Inc., Taiwan), Maillard browning, concentration of sugar and pyruvaldehyde.

2.2. Galatose/glycine model system

Experiment procedures were the same as glucose/glycine model system with α-D(+)-galactose (Sigma Chemical Co., USA) instead of α-D(+)-glucose.

2.3. Measurement of color change

The color change of model systems was measured using two parameters: absorbance at wavelength 420 nm (A_{420}) and Hunter L, a, b value. Instrument for determining A_{420} was a spectrophotomerer (U-1100, Hitachi, Japan), while that for Hunter L, a, b was a colorimeter (U-3000, Hitachi, Japan).

2.4. Determination of sugar concentration

Sugar concentration of sample solution was determined using HPLC. After filtration, 10 μl sample was fractionated in a NH_2 column (4 mm ID × 250 mm, 5 m particle size; Lichrosorb NH_2, Merck, Germany) using acetonitrile/water (80/20) as mobile phase eluting at a rate of 1.2 ml/min. Sugar peaks were detected by a RI detector (L-3500 RI-monitor detector, Hitachi, Japan), and calculated using a software (D-6000 Chromatography Data Station Software, Hitachi, Japan) installed in an IBM compatible PC (Acer Inc., Taiwan).

2.5. Determination of pyruvaldehyde

Pyruvaldehyde is a water soluble, highly active compound. It reacts readily with compounds primary amine, acetaldehyde and so on. That makes direct GC analysis of pyruvaldehyde very difficult. Hayashi and Shibamoto (1985) developed a method involving derivation of pyruvaldehyde with cysteamine. In the current study, determination of pyruvaldehyde followed their procedure with some modification because of its very low concentration in our model systems.

For qualitative analysis of pyruvaldehyde, cysteamine hydrochloride (0.75 g) was added to 100 ml of de-ionized water that contained 2.5μl pyruvaldehyde (Sigma Chemical Co., USA). The mixture was then adjusted to pH 6.0 using 0.1 N NaOH, stirred for 30 min at room temperature, and extracted by dichloromethane for 6 hr in a liquid-liquid extractor. The extract was dehydrated by anhydrous sodium sulfate overnight in a refrigerator, and then concentrated in 65 °C water bath to a volume less than 0.5 ml. The concentrate was then fractionated in a DB-Wax fused silica capillary column (30 m × 0.25 mm, J&W Scientific, USA) installed in a GC (model Autosystem, Perkin–Elmer, USA), using helium carrier gas at a flow pressure of 7.6 psi. The setting conditions for GC analysis were: oven temperature held at 80 for 5 min, programmed at 3 °C/min to 200 °C and held for 10 min. Chemical structures of these fractions were detected using a Mass Spectrometer (Q-Mass 910, Perkin–Elmer, USA) equipped with NIST data library. Analytical conditions for mass spectrometry were set as follow: helium carrier gas flowed at pressure 7.6 psi, the temperature of ion source was 150 °C, and ion voltage was 70 eV.

For quantitative analysis, sample concentrate was prepared from 100 ml of sample solution, added with 500 μl internal standard (20% w/v *N*-methylacetamide). The sample concentrate was then fractionated and detected using the same GC equipped with a FID. The relative amounts of fractionated peaks were calculated using an integrator (model 1020, Perkin–Elmer, USA).

2.6. Data analysis and statistical method

Absorbance at wavelength 420 nm (A_{420}) and difference of color index (ΔE) were used to indicate browning of the model systems. Values of ΔE were calculated using the following equation (Zamora & Hidalgo, 1992):

$$\Delta E = \{(\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2\}^{1/2}. \quad (1)$$

Rates of reaction including browning and sugars consumption were calculated using equation:

$$v = -d[\mathrm{R}]/d\mathrm{t} = k[\mathrm{R}]^n \quad (2)$$