KOREAN J. FOOD SCI. TECHNOL.
Vol. 16, *No.* 2 (1984)

Browning Pattern and Pigment of Glucose/Glycine Model Systems

Sang-Sook Nam and Mie-Soon Lee Kim

Department of Food and Nutrition, Duksung Women's College, Seoul

글루코스-글리신 혼합용액의 갈색화 패턴 및 색소

남상숙 · 이미순

덕성여자대학 식품영양학과

Abstract

Browning pattern was developed in aqueous solutions of glucose/glycine mixture under controlled conditions. Browning pattern was definitely influenced by pH of medium and concentration of reactants. Filter paper disks were immersed in diluted solutions of glucose/glycine system and fried in cooking oil. Concentrations of reactants only affected browning pattern of fried filter paper disks and pH effect was obscured at high temperatures. Amorphous brown precipitate was obtained from the lowest pH medium of glucose/glycine system. An attempt was made to characterize the brown pigment produced in the present model system.

Introduction

The increasing demand of potato chips encourages research on the processing quality of potato tubers recently in Korea. In potato chip processing, color is the most important factor influencing the quality of the product. It is well known that color of potato chips depends upon the reaction of reducing sugar and amino acid. Potato tubers stored at low temperature to prevent sprout growth accumulate reducing sugar and it makes chip color undesirable.[1].

The processing quality of Korean potato varieties for chip production[2-4] had been studied in our laboratory. As a result of reconditioning low-temperature stored potatoes at room temperature, the decreased patterns of reducing sugars were varied depending upon the varieties.

In general, the change of reducing sugar is only considered as an important problem for chip color of potatoes which have been stored at low temperature, since potato tubers contain always sufficient amount of amino acid for color formation[1]. Accordingly the reproducible test procedure for aminocarbonyl reaction was required, as a preliminary step to investigate chip color and its brown pigment.

In our laboratory, a filter paper disk technique was employed to evaluate the browning reaction in potato chips fried at 170 °C. In the potato extracts the filter paper disks were immersed and fried at 170 °C. The color of the filter paper well reflected that of potato chip.

The present experiment was undertaken to investigate browning patterns of glucose/glycine solutions at various concentrations and pHs along with the evaluation of the browning degree by filter paper disks.

Materials and Methods

The reactants for browning development were glucose and glycine of Merck Company. The reaction mixture included aqueous glucose/glycine solution at 1% molar ratio. A 10*ml* of mixed glucose/glycine solution was placed in the test tube and incubated at 90 °C water bath for required time. The pH of the reaction mixture was adjusted to 2, 4, 6 and 8 with HCl or NaOH. The ex-

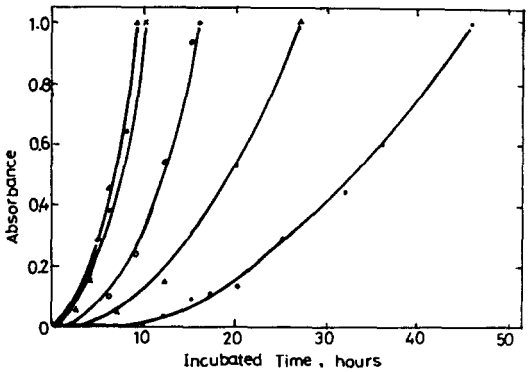

Fig. 1. Browning pattern of aqueous solutions containing various concentration of glucose /glycine (△—△; 1.0*M*/0.5*M*, ×—×; 0.8*M*/0.4*M*/○—○; 0.6*M*/0.3*M*, ▲—▲; 0.4*M*/0.2*M*, ●—●; 0.2*M*/0.1*M*)

tent of browning development was determined by measuring absorbance at 420*nm*.

Varied mixing ratios of glucose/glycine solution were also used for the investigation of browning pattern. They were prepared by combining equal amount of doubled concentration of glucose or glycine solution mutually. Influence of temperature on browning reaction was examined by incubating test tubes at 50 °C and 90°C water bath. Browning patterns as influenced by concentration or pH of glucose/glycine solution are examined by the following procedures. Filter paper disks were immersed in serially diluted, aqueous glucose (0.6*M*)/glycine(0.3*M*) solution whose pH is 2, 4, 6 and 8, and then fried in cooking oil at 170 °C.

UV absorption spectra were measured with 1.0 *M*/0.5 *M* glucose/glycine solutions of pH 2 and pH 8 which have been incubated for 10 or 20 hours at 90 °C, using UV spectrophotometer(Model SP 200; Shimazu-kyoto, Japan). Dark brown amorphous substance was precipitated from 1.0 *M*/0.5 *M* glucose/glycine solution of pH 2 after 120 hours reaction. The precipitate was kept at room temperature for 5 days. It was collected from centrifugation and air-dried at room temperature for 5 hours. Prepared precipitate was further dried for 4 hours in vaccum drying oven at 25 °C and ground to fine powder. Infrared spectrum was recorded on a Perkin-Elmer Model SP 710B spectrophotometer in pressed disks of KBr.

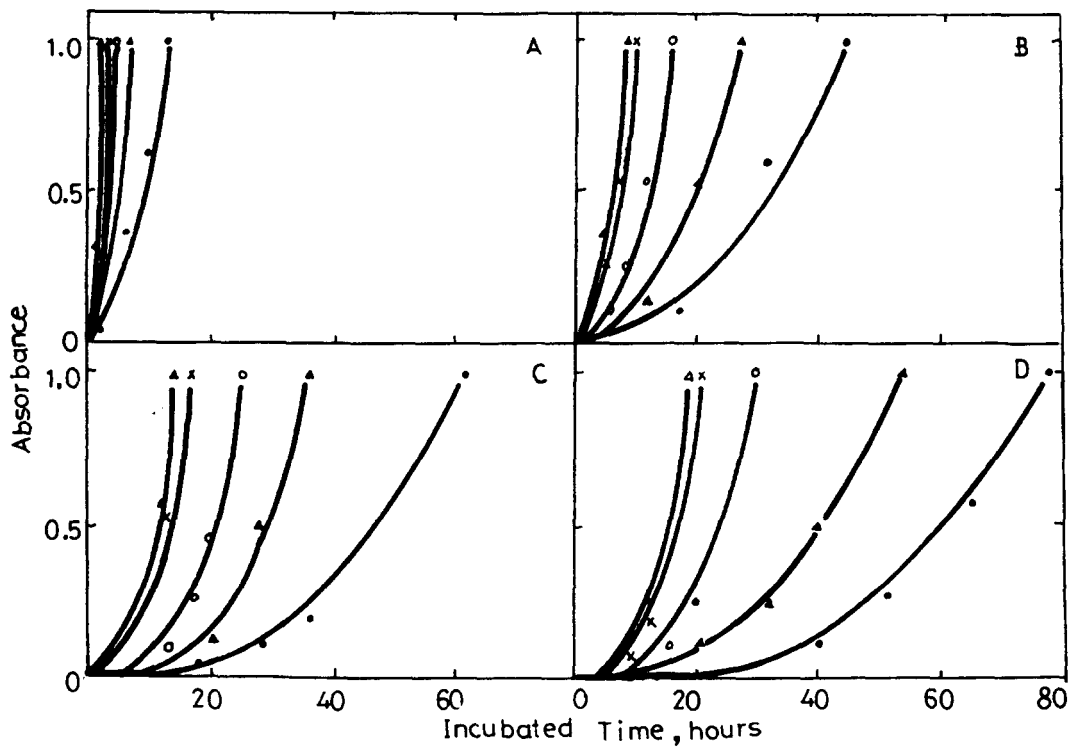

Fig. 2. Browning pattern of glucose/glycine solution at pH 8(A), pH 6(B), pH 4(C), pH 2(D) (△—△; 1.0*M*/0.5*M*, ×—×; 0.8*M*/0.4*M*, ○—○; 0.6*M*/0.3*M*, ▲—▲; 0.4*M*/0.2*M*, ●—●; 0.2*M*/0.1*M*).

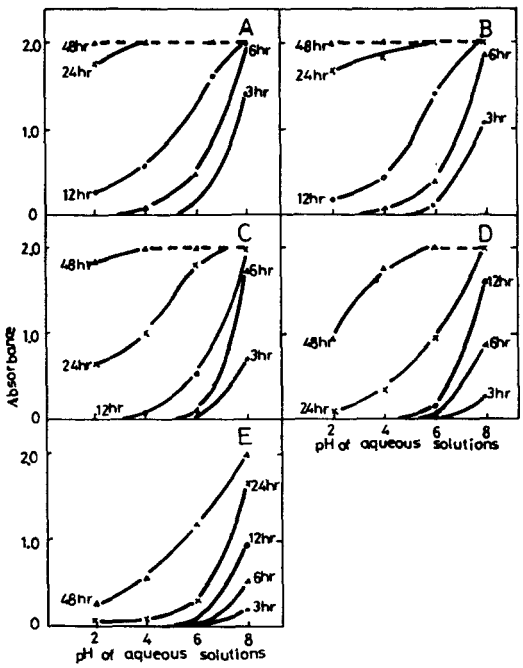

Fig. 3. Browning pattern of glucose/glycine solutions as influenced by pH of aqueous solutions
(A) 1.0*M*/0.5*M*; (B) 0.8*M*/0.4*M*;
(C) 0.6*M*/0.3*M*; (D) 0.4*M*/0.2*M*;
(E) 0.2*M*/0.1*M*.

Results and Discussion

Fig. 1 shows browning pattern of aqueous solutions containing various concentrations of glucose/glycine. Browning was rapidly proceeded with increasing concentrations of glucose/glycine solution. The 1.0 *M* / 0.5 *M* and 0.8 *M* /0.4 *M* glucose/glycine solutions showed severe browning reaction within 10 hours. The lowest concentration of glucose/glycine solution required approximately 2 days to reach maximum absorbance. It has been reported that the rate of browning reaction is significantly affected by the concentration of reactants.[5] According to Wolfrom et al.[6] browning was rapidly developed as the mole number of glucose became higher, when mixed solutions of glucose/arginine had varied molar ratios such as 1/1, 2/1, 4/1 and 10/1.

Browning patterns of various concentrations of glucose/glycine solutions at different pH are shown in Fig. 2. All concentrations of glucose/glycine solution revealed rapid browning at pH 8. The 1.0 *M* /0.5 *M*, 0.8 *M* / 0.4 *M* and 0.6 *M* /0.3 *M* glucose/glycine solutions reached maximum absorbance after 5 hours reaction. Even the lowest concentration of glucose/glycine solution showed severe browning of maximum absorption after 15 hours reactions. Apparently, the identical concentration of glucose/glycine solution developed browning more slowly as pH of the solution became lower. From Fig. 2, it is clear that the reaction rate of browning was remarkably influenced by pH. Browning reaction rapidly occurs as pH of the solution became higher,[5,7,8] and is best inhibited by lowering the pH.[9]

The 1.0 *M* /0.5 *M* glucose/glycine solution reached maximum degree of browning after 6 hours reaction, while the 0.8 *M* /0.4 *M* and 0.6 *M* /0.3 *M* glucose/glycine solution after 12 hours(Fig. 3). Maximum degree of browning was obtained in lower concentrations of glucose/glycine solution such as 0.4 *M* /0.2 *M* and 0.2 *M* / 0.1 *M* after 24 or 48 hours reaction.

In Fig. 4, the degree of browning was manifested at various concentrations of glucose and glycine. Under the present experimental conditions, the degree of browning was more definitely influenced by limited amount of glycine rather than glucose[1,10]. The degree of browning tended to increase as the concentration of glucose and/or glycine became higher. However, the trend of increased browning was not so distinct in the upper ranges of glucose and glycine concentrations. McWeeny and Burton[11] reported that glycine accelerated

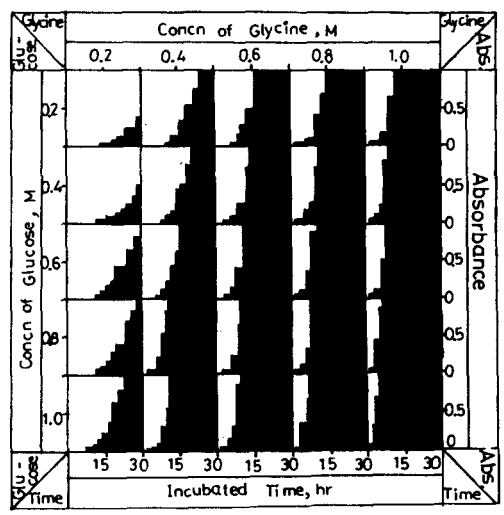

Fig. 4. Degree of browning as affected by the combination of various concentrations of glucose and glycine

browning more than glucose. Warmbier et al.[12] investigated the kinetics of nonenzymatic browning reactions, varying molar ratios of glucose and lysine. According to these workers, glucose/lysine solution produced plateau for the extent of browning above 3/1 molar ratio.

The fact that temperature affects browning reaction has been well established[13]. As shown in Table 1, the times required for browning at the reaction temperature of 90 °C are only 1/15-1/6 of those at 50 °C. In the present study, the time required for browning of definite absorbance of 0.5-1.0 was examined.

Fig. 5 shows browning pattern of fried filter papers as influenced by diluted concentrations of glucose/glycine in aqueous solutions. The color of fried filter papers showed the same degree of browning at far lower concentration of glucose/glycine solution that the one reacted in test tubes. Little or no color developed in fried filter paper disks, with glucose alone or glycine alone[1]. It is distinctly shown that darker filter paper disks were produced as original concentrations of glucose/glycine solution became higher. The more diluted, the lighter filter paper disks were produced.

Browning pattern of fried filter papers as influenced by pH of diluted 0.6 *M* /0.3 *M* glucose/glycine solution is shown in Fig. 6. As shown in this figure, fried filter papers revealed the same degree of browning at different pHs. This result implied that the effect of pH on Maillard

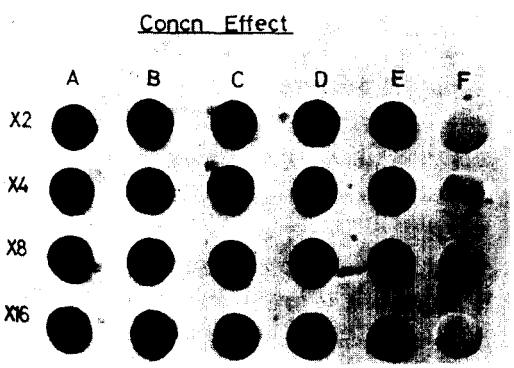

Fig. 5. Browning pattern of fried filter papers as influenced by × 2, × 4, × 8 or × 16 diluted concentrations of glucose/glycine in aqueous solutions

(A) 1.0*M*/0.5*M*; (B) 0.8*M*/0.4*M*; (C) 0.6 *M*/0.3*M*; (D) 0.4*M*/0.2M; (E) 0.2*M*/0.1 *M*; (F) Control.

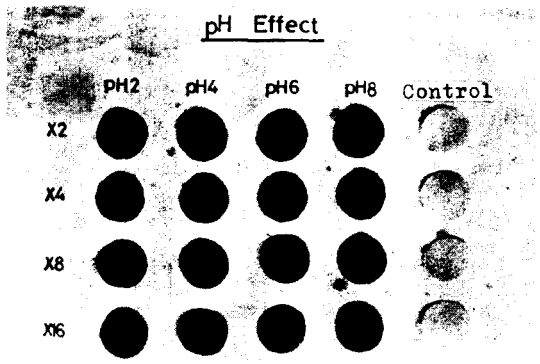

Fig. 6. Browning pattorn of fried filter papers as influenced by pH of × 2, × 4, × 8, or × 16 diluted 0.6*M*/0.3*M* glucose/glycine solution

reaction was obscured at high temperature of frying.

UV absorption spectra of 1.0 *M* /0.5 *M* glucose/glycine solution were measured at pH 8 and pH 2 after 20 hours reaction(Fig. 7). A new absorption peak which has not been existent prior to the reaction of mixed glucose/glycine solution was observed at 283*nm* and considered to be due to conjugated carbonyl compounds[14,15]. UV absorption of glucose/glycine solution was approximately 7 times greater at pH 8 than at pH 2 after 10 hours reaction. The degree of visible browning tended to increase at pH 2 after 10 hours reaction, even though maximum absorbance was shown at pH 8 within 10 hours(Fig. 2 and Table 2). Therefore, it is presumable that the increasing rate of UV absorption is somewhat correlated to the progress of browning[14].

Infrared spectrum of the browned amorphous precipitate obtained from the reaction mixture of 1.0 *M* / 0.5 *M* glucose/glycine at pH 2 is shown in Fig. 8. In-

Table 1. Effect of incubation temperatures on the browning pattern of aqueous solutions of glucose/glycine mixture

Treatments	Approximate time required to show identical degree of browning (hr)			
	Absorbance			
	0.5		1.0	
	90℃	50℃	90℃	50℃
Glucose/glycine:				
0.2*M*/0.1*M*	33	—	44	—
0.4*M*/0.2*M*	20	240	27	—
0.6*M*/0.3*M*	12	170	16	240
0.8*M*/0.4*M*	7	60	10	88
1.0*M*/0.5*M*	6	38	9	56

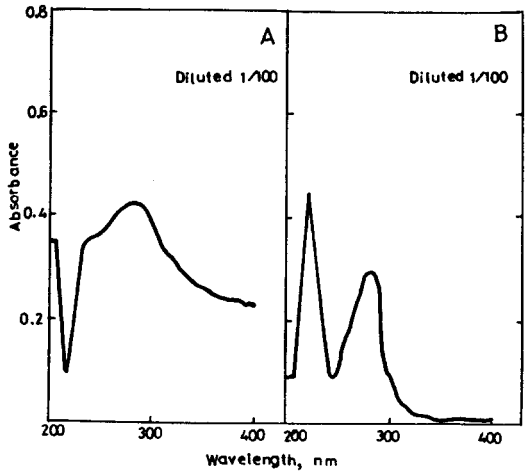

Fig. 7. UV spectra of the browned solution after 20 hours incubation of 1.0*M*/0.5*M*/glucose /glycine at pH 8(A) and pH 2(B)

frared spectrum shows peaks of—OH bond at 3280cm^{-1}, double bond at 1622cm^{-1} and–C=O bond at 1040cm^{-1}. The infrared spectrum is very similar to the one of the brown precipitates from the reaction of glucose/aspartic acid solution or of brown pigment extracted from baked barley[16].

요 약

조정된 조건하에서 glucose－glycine 혼합수용액을 사용하여 browning을 발달시켰다. Browning pattern은 medium의 pH 및 반응물질의 농도에 특히 영향을 받았다. Glucose－glycine수용액을 회석시켜 filter paper disks를 담갔다가 기름으로 튀겼다. 반응물질의 농도는

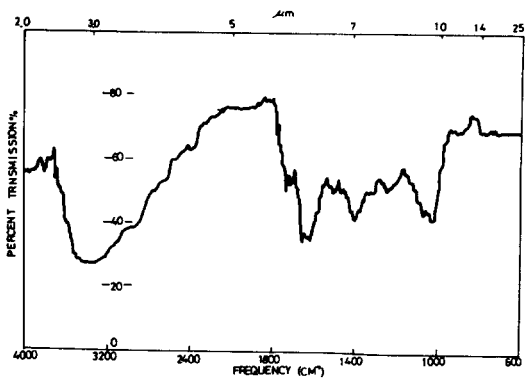

Fig. 8. Infrared spectrum of the browned amorphous precipitate obtained from the reaction mixture of glucose and glycine at pH 2

Table 2. The comparative UV absorption at 283*nm*

Incubation time	pH 2	pH 8
10 hr	1	7
20 hr	5.4	7.7

튀긴 filter paper disks의 browning pattern에만 영향하고 pH 영향은 고온에서 불명확하게 되었다. Glucose－glycine system의 pH 2에서는 무결정형의 갈색 침전물이 생성되었다. 본 model system에서 생성된 갈색색소를 규명하기 위하여 기기분석을 시도하였다.

References

1. Smith, O.: *Potato Processing*, AVI Publishing Co., Westport, CT., p. 224 (1967)
2. 李美淳：덕성여자대학 논문집, 5, 6집, 325 (1977)
3. 李美淳：한국 작물개량연구소 보고 (1977)
4. 李美淳：한국 작물개량연구소 보고 (1978)
5. Lea, C. H. and Hannan, R. S., :*Biochim. Biophs. Acta.*, 3, 313 (1949)
6. Wolfrom, M. L., Kashmura, N. and Horton, D. :*J. Agric. Food Chem.*, 22, 796 (1974)
7. Wolfrom, M. L., Kolb, D. K. and Langer, Jr. A. W. : *J. Am. Chem. Soc.*, 75, 3471 (1953)
8. 梁隆, 申東範：한국식품과학회지, 12, 88 (1980)
9. Fennema, O. R. :*Food Chemistry*, Mercel Dekker Inc., New York, Vol. 4, p. 86 (1976)
10. Burton, H. S., McWeeny, D. J. and Biltcliffe, D.O.: *J. Food Sci.*, 28, 63 (1963)
11. McWeeny, D. J. and Burton, H. S. :*J. Sci. Food Agric.*, 14, 29 (1963)
12. Warmbier, H. C., Schnikels, R. A. and Labuza, T. P. :*J. Food Sci.*, 41, 981 (1976)
13. Stamp, J. A. and Labuza, T. P. :*J. Food Sci.*, 48, 543 (1983)
14. Tan, T. L., Wolfrom, M. L. and Langer, Jr. A.W.: *J. Am. Chem. Soc.*, 72, 5090 (1950)
15. Dillard, C. J. and Tapple, A. L. :*J. Agric. Food Chem.*, 24, 74 (1976)
16. Milic, B. Lj., Grujic－Injac, B., Piletic, M. V., Lajsic, S. and Kolarov, Lj. A. :*J. Agric. Food Chem.*, 23, 960 (1975)

(Received March 20, 1984)