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Effects of Caffeic Acid on the Rates of Maillard Reaction

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마이얄반응속도에 미치는 카페인산의 영향

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요 약

본 연구에서는 마이얄반응속도에 미치는 카페인산의 영향을 조사하고자 하였다. 갈색화 반응속도는 60와 80℃에서 매우 느리게 나타났으나, 100℃에서 크게 증가하였다. 갈색화반응속도는 환원당보다는 아미노산의 종류에 의해 더 큰 영향을 받았다. 또한 카페인산가 첨가될 때 갈색화반응물의 색깔의 강도는 증가되었으며 이러한 증가는 주로 카페인산으로 부터 형성된 o-quinones의 중합에 기인되는 것으로 생각되었다. 더욱이 카페인 산과 아미노산, 특히 phenylalanine이나 methionine과의 상호반응에 의해 색깔의 강도는 더욱 증가하는 것으로 나타났다. 카페인산이 첨가되지 않은 갈색화반응물의 활성화에너지는 108~130 J/mol정도, 온도계수(Q_{10} value)는 2.6~3.2정도였으며 카페인산의 첨가에 의해 갈색화 반응의 활성화에너지는 상대적으로 낮아졌다. 카페인산이 첨가된 갈색화반응의 활성화에너지는 80~101 J/mol정도, 온도계수는 2.0~2.6정도였다.

Abstract

It was aimed to investigate the effects of caffeic acid on the rates of Maillard reaction. The rates of browning reaction increased as the browning temperature increased. The color intensity of the browning mixtures indicated to depend on the amino acid rather than reducing sugar. Also, the color intensity of the browning mixtures increased more rapidly in the presence of caffeic acid. The increase in color intensity seemed to depend mainly to the polymerization of o-quinones formed from caffeic acid. The caffeic acid, furthermore, appeared to enhance the color intensity of the browning mixtures through the interaction with amino acid, especially methionine and phenylalanine. The activation energies of the browning reaction without caffeic acid were 108~130 J/mol, and Q_{10} values were 2.6~3.2.

The activation energies and Q_{10} values of browning mixtures decreased in the presence of CA. The activation energies of the browning mixtures with caffeic acid were 90~101 J/mol, and Q_{10} values were 2.0~2.6.

I. Introdiction

The majority of browning pigments are formed through thermal interaction of reducing sugar and amino acid, known as the Maillard reaction. The rates of Maillard reaction are influenced in the first place by the nature of the reacting reducing sugar and amino acid[1].

Also, phenolic compounds that present in almost all plant-derived food products play an important role in the development of browning reaction[2,3]. Some workers[4-7] have reported the phenolic acids such as chlorogenic and caffeic acid(CA) undergo browning. Sosulski[8] has reported that the o-quinones result from the oxidation of caffeic acid are highly reactive, and as a singular or polymerized form, the o-quinones can bind with amino, thiol and methylene groups of proteins in foods. Torres *et al*[9]. have reported that phenolic acids commonly occur as esters or ethers in combination with sugars and aliphatic or aromatic acids and hydroxy acid. Therefore, it seems that the presence of caffeic acid and its derivatives in foods can directly or indirectly participate with sugar or amino acid in Maillard reaction. Although the effect of caffeic acid on the browning reaction has been studies, most works have been concentrated on enzymatic browning reaction. Furthermore, the effects of caffeic acid on the rates of Maillard reaction are still not well explained. In the present study, an attempt was made to investigate the effects of caffeic acid on the rates of Maillard reaction using sugars and amino acids at 60, 80 and

100℃, respectively.

II. Materials & Method

1. Materials

The sugars: glucose, fructose and xylose(Junsei Chemical Co., Japan), and the amino acids: glycine, methionine, phenylalanine and histidine(Sigma Chemical Co., U.S.A.) were chosen for this study.

The phenolic acid used in this study was caffeic acid (Sigma Chemical Co., U.S.A.).

2. Preparation of a Maillard browning mixtures

The rates of Maillard reaction was investigated in the glycine-sugar and glucose-amino acid browning mixtures with or without caffeic acid(CA). Aqueous mixtures of sugar(0.2 M) and amino acid(0.2 M) were introduced into capped tubes, and kept at 60, 80, and 100℃, respectively for 24 hrs. Each browning mixture was adjusted to pH 6.5 with 0.1 N NaOH or 0.1 N HCl prior to heating. Caffeic acid was added in browning mixture at concentration of 0.002 M. Each browning mixture was filtered and the color intensity at 420 nm of the filtrate was measured with Beckman UV/visible spectrophotometer.

3. The residual contents of sugar and amino acid in browning mixtures

The residual contents of sugar in browning mixtures heated at 100℃ for 24 hrs were determined by HPLC (Waters 501, U.S.A.). Also, amino acid contents were analyzed by means of automatic amino acid analyzer (LKB Biochrom alpha plus 4151 amino acid Autoanalyzer, England).

4. The activation energies(Ea) and temperature coefficients(Q_{10} values)

The rate constants were determined by using the following equation of the browning pigment concentration with time.

$$C = C_o + kt \quad (1)$$

where, C = brown pigment concentration(OD/hr × 10^3) at time t

C_o = brown pigment concentration at time t_o

k = rate constant(OD/hr)

t = reaction time(hr)

The activation energies(Ea) were obtained by plotting the log k against the reciprocal of the absolute temperature, according to the arrhenius equation.

$$\log k = \log k_o - \frac{Ea}{2.303R} \times \frac{1}{T} \quad (2)$$

where, k = rate constant

k_o = a pre-exponential(absolute) rate constant

T = absolute temperature(K)

Ea = activation energy(J/mol)

R = gas constant(J/mol K)

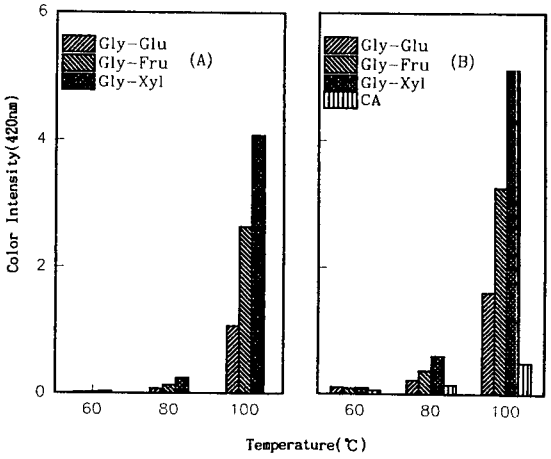

Fig. 1. The color intensity of the glycine-sugar browning mixtures without(A) or with(B) caffeic acid heated at various temperature for 24 hrs.

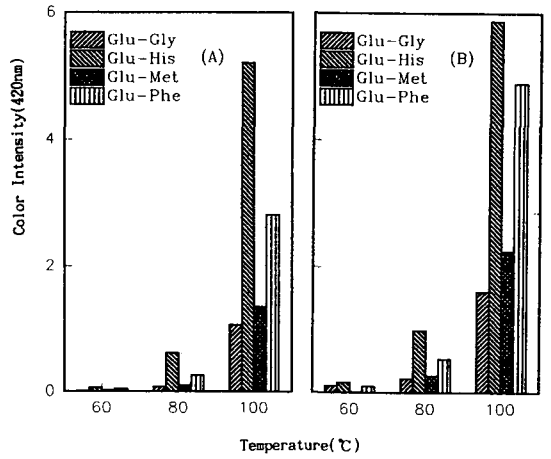

Fig. 2. The color intensity of the glucose-amino acid vowning mixtures without(A) or with (B) caffeic acid heated at various temperature for 24 hrs.
or with(B) caffeic acid heated at various temperature for 24 hrs.

Table 1. The residual contents of sugar and amimo acid in the browning mixtures heated at 100°C for 24 hrs

Reaction system	Residual content(%)	
	sugar	amino acid
Gly-Glc	70.4	79.4
Gly-Fru	65.0	77.4
Gly-Xyl	49.0	64.7
Gly-Glc-CA[a)]	69.0	59.5
Gly-Fru-CA	63.0	57.2
Gly-Xyl-CA	51.0	54.9
Glc-Gly	70.4	79.4
Glc-His	31.4	55.1
Glc-Met	66.8	83.0
Glc-Phe	63.4	78.2
Glc-Gly-CA	69.0	59.5
Glc-His-CA	31.0	39.6
Glc-Met-CA	66.0	64.6
Glc-Phe-CA	63.0	43.5

[a)] Gly-Glc-CA=glycine-glucose-caffeic acid browning mixtures

The temperature coefficients(Q_{10} value) were derived from the activation energies utilizing the equation below.

$$\log Q_{10} = \frac{2.2\ Ea}{T(T+10)} \quad (3)$$

where, $Q_{10}=Q_{10}$ Value

Ea=activation energy(J/mol)

III. Results and Discussion

1. The color intensity of the browning mixtures

The color intensity of the browning mixtures heated at 60, 80, and 100℃, respectively, for 24 hours in shown in Fig. 1 and 2. The color intensity of the browning mixtures with or without caffeic acid(CA) increased as the browning temperature increased. The color intensity of the browning mixtures heated at 60℃ and 80℃ increased slowly, while that of the mixtures heated at 100℃ increased rapidly.

The color intensity in the glycine-sugar browning mixtures decreased in order of xylose>fructose>glycine. In the glucose-amino acid browning mixtures, the color intesity decreased in order of histidine>phenylalanine>methionine>glycine. These results indicated the rates of browning reaction are influenced by the type of the reducing sugar and amino acid involved in browning reaction.

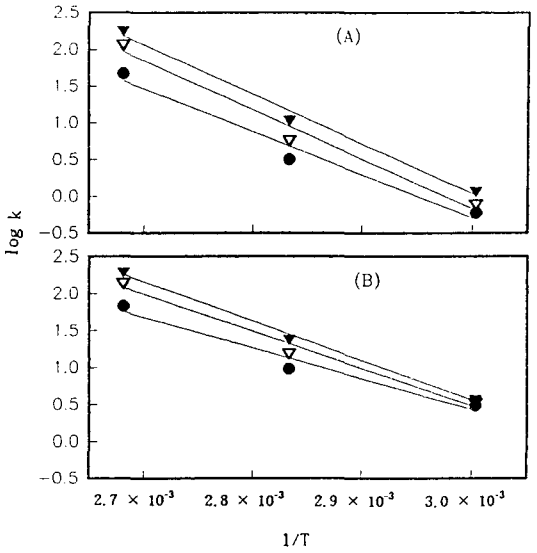

Fig. 3. Arrhenius plot of rate constant of the glycine-sugar browning mixtures without(A) of with (B) caffeic acid Vs reciprocal absolute temperature.

● Gly-Glu, ▽ Gly-Fru, ▼ Gly-Xyl

Also, when CA was added to the browning mixtures, a significant increase in the color intensity was observed. The increase in color intensity was greater in glucose-amino acid browning mixtures than in glycine-sugar mixtures. Therefore, when CA was added in the browning mixtures, the increase in color intensity was seemed to depend on the amino acid, especially methionine and phenylalanine rather than that of reducing sugar.

As can be seen in Fig. 1(B), it appears that CA alone undergoes browning in aqueous solution. Torres *et al.*[9] have suggested that CA can be oxidized atmospherically to o-quinone, which in turn polymerized and produced browning pigment.

Therefore, when CA added to the browning mixtures, the increase in color intensity seemed to be due primarily to the polymerization of o-quinines formed from CA. The caffeic acid, furthermore, appeared to enhance the color intensity of glycine-sugar and glucose-amino acid browning mixtures. This tendency was more pronounced in the glucose-amino browning mixture. It seemed that interaction of caffeic and amino acid was involved in formation of browning pigment. The residual contents of sugar and amino acid in browning mixtures

The residual contents of sugar and amino acid in browning mixtures heated at 100℃ for 24 hrs are

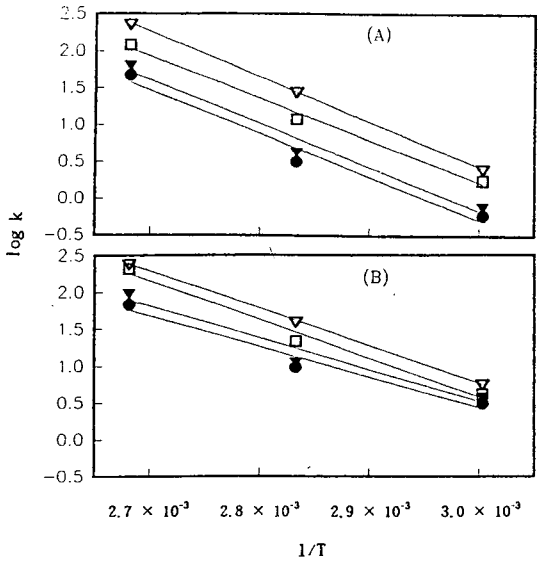

Fig. 4. Arrhenius plot of rate constant of the glycine-sugar browning mixtures without(A) of with (B) caffeic acid Vs rescipal absolute temperature.
● Glu-Gly, ▽ Glu-His, ▼ Glu-Met, □ Glu-Phe

shown in Table 1.

In case of the glycine-sugar browning mixtures without CA, the residual contents of glucose, furctose and xylose were 70.4, 65.0 and 49.0%, respectively. These results indicated that xylose was severely decomposed, whereas glucose and fructose were not decomposed so much.

When CA was added in the glycine-sugar browning mixtures, the residual contents of glucose, fructose and xylose were 69.0, 63.0 and 51.0%, respectively. This result showed that the residual contents of sugars had no great difference in the presence of CA.

Therefore, although the color intensity of glycine-sugars browning mixtures increased more quickly in the presence of CA, it is not likely that CA affect decomposition of sugars involved in glycine-sugars browning mixtures.

On the other hand, the residual contents of glycine in glycine-sugar browning mixtures were 64~80% in the absence of CA and 54~60% in its presence. It indicated that the decomposition of glycine was more easily occuring in the presence of CA. Cabanes *et al.*[10] have reported that o-quinone possesses strong electophilic nature and thus easily undergoes attack by nucelophiles. Cheynier *et al.*[11]have also reported that the benzene ring in CA in the most electrophilic, and nucleophilic addition occurs preferentially here.

Table 2. Rate constants(k), activation energies(Ea) and Q_{10} values of the browning mixtures

Browning mixture	Rate constant			Activation	Q_{10} value
	60℃	80℃	100℃	(J/mol)	90~100℃
Gly-Glc	0.6	3.2	47.8	112.50	2.73
Gly-Fru	0.8	5.9	120.1	128.88	3.16
Gly-Xyl	1.2	11.1	184.0	129.63	3.18
Glc-Gly	0.6	3.2	47.8	112.50	2.73
Glc-His	2.6	28.8	236.2	116.52	2.83
Glc-Met	0.8	4.4	65.9	113.38	2.75
Glc-Phe	1.8	12.1	122.6	108.74	2.64
Gly-Glc-CA[a)]	3.1	9.6	68.8	79.59	2.04
Gly-Fru-CA	3.4	15.9	142.8	96.18	2.36
Gly-Xyl-CA	3.8	24.8	213.7	103.88	2.53
Gly-Gly-CA	3.1	9.6	68.8	79.59	2.04
Gly-His-CA	5.8	40.3	250.2	97.22	2.38
Glc-Met-CA	3.9	11.5	98.6	82.86	2.10
Glc-Phe-CA	4.2	21.7	210.6	100.74	2.46

a) Gly-Glc-CA=glycine-glucose-caffeic acid browning mixtures

It seemed that the presence of nucleophiles such as amino acid lead to the interaction with o-quinones result from the decomposition of CA. Therefore, the accelerated decomposition of glycine was considered to be due to the formation of complexes by interaction of CA or its oxidative products and amino acid.

In case of the glucose-amino acid browning mixtures without caffeic acid, the residual contents of glycine, histidine, methionine and phenylalanine were 79.4, 55.1, 83.0 and 78.2%, respectively.

This reault indicated that not all amino acids are equally reactive with glucose, i.e., histidine are more susceptible to degradation than glycine, methionine or phenylalanine. It would be considered that the histidine are decomposed more easily than others because of the presence of a relatively basic nitrogen atom in the side chain[12].

When CA was added in the glucose-amino acid browning mixture, the residual contents of glycine, histidine, methionine and phenylalanine were 59.5, 39.6, 64.6 and 43.5%, respectively.

These results indicated apparently that amino acids, especially phenylalanine and methionine were decomposed more rapidly in the presence of CA. Therefore, it seemed that phenylalanine and methionine are more susceptible to interaction with CA than glycine or histidine.

2. Rate constant, activation energies and Q_{10} value

The effects of temperature on the rates of browning mixtures expressed by the Arrhenius plots are shown in Fig. 3 and 4. The log k was plotted against the reciprocal of the corresponding the absolute temperature. As shown in Fig. 3 and 4, the log k and the reciprocal of the absolute temperature showed linear relationships.

It was found that the Arrhenius plots can be applied to the effects of temperature on the rates of browning mixtures. Rate constants, activation energies and temperature coefficients(Q_{10} value) of Maillard reaction mixtures are shown in Table 2.

The activation energies of the browning mixtures without CA were 108~130 J/mol, and Q_{10} values were 2.6~3.2. When CA was added to the browning mixtures, the activation energies of the browning mixtures were 90~101 J/mol, and Q_{10} values were 2.0~2.6. Therefore, the activation energies and Q_{10} values of browning mixtures decreased in the presence of CA.

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