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Thermal Kinetics of Gamma–Aminobutyric Acid and Antioxidant Activity in Germinated Red Jasmine Rice Milk using Arrhenius, Eyring-Polanyi and Ball Models

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Abstract

The thermal kinetics of changes of γ–aminobutyric acid (GABA) and antioxidant activity (DPPH assay) in germinated red jasmine rice milk (GRJM) at heating temperatures of 80, 90, 100 and 121°C using Arrhenius, Eyring–Polanyi and Ball models was examined in this study. Under isothermal conditions, the increasing of heating temperature from 80°C to 121°C resulted in the decreasing of GABA. However, DPPH radical scavenging activity increased under temperature range of 80–100°C, but decreased at 121°C. The highest residue of GABA was 94% after heatingat 80°C for 30 min, while the highest increasing of DPPH radical scavenging activity was 230% at 90°C for 30 min. Thermal degradation of GABA followed a second–order reaction kinetic, while the increasing of antioxidant activity (80–100°C) followed a first–order kinetic as well as the degradation of antioxidant activity (121°C). The heating temperature dependence of rate constant for degradation of GABA and increasing of antioxidant activity were described by Arrhenius, Eyring–Polanyi and Ball models. Following the Arrhenius law, activation energies were 59.62 kJ/mol and 30.31 kJ/mol, respectively for degradation of GABA (80–121°C) and increasing of antioxidant activity in GRJM (80–100°C). Arrhenius, Eyring–Polanyi and Ball models could be used to predict accurately GABA content and antioxidant activity in GRJM during isothermal heat treatment.

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Introduction

Red jasmine rice (Hom Mali Deang) is a color brown rice variant[1,2] and a potent source of antioxidants with health benefits such as anthocyanins, flavones and flavonols, carotenoids and γ–oryzanols.[3] It also possesses higher antioxidant activitythan those of other brown rice varieties[1] and black pigmented rice (KamLeumPua).[4]

Moreover, germinated rice is enriched with functional ingredients, particularly γ–aminobutyric acid (GABA) during germination process.[5,6] GABA is a non–protein amino acid, is an inhibitory neurotransmitter in the central nervous system.[7] GABA exhibits many biological activities including anti–hypertensive effect, accelerating metabolism in brain, preventing Alzheimer's disease and regulation of cardiovascular function.[6,8] Wichamanee and Teerarat[2] reported that the germinated red jasmine rice contained much higher concentrations of GABA than that in ungerminatedred jasmine rice.

A functional beverage such as germinated red jasmine rice milk (GRJM) is a good source of GABA and has antioxidant activity. However, heating is often used in food processing to extend shelf life but it can destroy heat–unstable compounds, especially functional ingredients like GABA[9] and may affect antioxidant properties of food products.[10,11] Khan *et al*.[9] found that GABA in *Monascus*–fermented rice solution decreased rapidly during heating, especially at high temperature of 121°C. In addition, the different heating conditions, namely temperature and period showed the different effects on antioxidative properties of foods.[7,12] The thermal degradation of antioxidative property has been reported in some plants such as green tea, eggplant and green pepper,[13] ground apples[14] and kiwifruit puree.[15] However, the positive effect of thermal treatment on antioxidant activity of food products has been also reported in many studies, for example, in onion,[10] beetroot,[13] citrus peel[12,16] and dragon fruit.[17]

The heating temperature is a very important parameter in order to obtain the maximum yields of functional ingredients and may impact to antioxidant activity. However, the influence of heating temperature on GABA content and antioxidant activity in GRJM has never been studied. The Arrhenius model is an empirical collision model that has been used wildly to describe temperature dependence of the chemical reaction rate. Eyring–Polanyi model can also be used to explain the influence of temperature on rate of chemical reaction to change in enthalpy and entropy terms based on transition state theory.[11,18] Often the Ball or Bigelow equation is applied in food processing to describe thermal resistance of functional ingredients in food systems[11,18] and microorganism inactivation.[19] Kinetic parameters are necessary to predict changes in nutritional quality with heating. Data from kinetic models can be utilized to develop the heat processing of GRJM. The aim of this work was to examine the effect of temperatures from 80°C to 121°C on GABA and antioxidant activity in GRJM. The thermal kinetics of changesof GABA and antioxidant activity in GRJM were described and evaluated on the basis of Arrhenius, Eyring–Polanyi and Ball models.

Materials and Methods

Materials

Germinated red jasmine rice (*Oryza sativa* L. cv. Hom Deang) was purchased from Bangkok Thai Rice Market Co., Ltd. (B–Herbs), Thailand. Longan honey was obtained from Bee Products Industry Co., Ltd, Thailand and xanthan gum food grade was obtained from Jungbunzlauer Austria AG, Austria.

Preparation of Germinated Red Jasmine Rice Milk

GRJM was ground in a blender and sieved through #80 meshes, mixed with water (1:15 by mass), heated to 50°C for 10 min to extract starch and consequently filtered through a double layer of cheesecloth leaving a product called GRJM.[20,21] A 0.08% of xanthan gum was added to improve stability. Sweetness was adjusted with 9.5% of longan honey on the basis of acceptability sensory testing with 30 untrained panelists using a 9–point hedonic scale. Total soluble solids (TSS) of GRJM were 8.0°Brix at 25°C (Master, Atago, Japan) and pH of 6.5 (UB–10, Denver Instrument, USA).

Heat Treatment

The effect of temperature on GABA and antioxidant activity of GRJM was measured at 80, 90, 100 and 121°C at a residence time of 0–30 min. Aliquots of 20 mL GRJM were put into screw–cap tubes and heated in a water bath at 80, 90 and 100°C (Model 11DT–1, Heto, Denmark) as well as in an autoclave (Model H–99LL, Kokusan, Japan) at 121°C. Samples were

removed immediately after thermal treatmentand then cooled in an ice water bath to minimize further reaction and frozen (-18°C) until analyzed. In case of the heating at 121°C, sample was taken out after releasing the pressure inside autoclave.

Extraction Procedure

GRJM (50 mL) was mixed with 100 mL of 70% (by volume) ethanol with a magnetic stirrer for 20 min and then centrifuged at 8000×g, 4°C for 5 min. The supernatant was collected and added with 100 mL of 70% (by volume) ethanol. The solution was mixed and again centrifugedas before. The ethanol in the supernatant was evaporatedunder vacuum at 40°C using rotary evaporator (RC 900, KNF Flodos AG, Switzerland). The concentrated extract was analyzed for GABA concentration and antioxidant activity.[4,7]

Determination of Gamma–aminobutyric Acid

GABA concentration was assayed by the spectrophotometric method described by Sharma *et al*.[7] Briefly, the concentrated extract (0.1 mL) was mixed with the reagent solution containing of 0.2 M borate buffer pH 9.0 (0.2 mL) and 6% phenol reagent (1 mL). A 7.5% solution of sodium hypochlorite (0.4 mL) was then added and together boiled for 10 min in a water bath. The sample was cooled under running tap water. Extract absorbance was conducted at 630 nm in a spectrophotometer (Genesys 20, Thermo Scientific, USA). The solvent was used as blank. A standard curve was prepared with GABA concentrations of 10-50 μg/mL and used for sample analysis. Sample values represented means of triplicate analyses.

Determination of Antioxidant Activity

DPPH radical scavenging activity was measured as a surrogate of antioxidant activity.[4,15] The concentrated extract (100 μL) was vortexed with 0.9 mL of 0.15 mM DPPH methanolic solution and stored for 30 min in darkness at ambient temperature. Absorbance of the mixture was monitored at 517 nm (Genesys 20 spectrophotometer, Thermo Scientific, USA). Absorbance of DPPH solution of the mix in which 100 μL distilled water instead of sample was employed as a control. Results were expressed as % DPPH radical scavenging activity (DPPH RSA), which was calculated according to the following equation (1):

$$\% \text{ DPPH RSA} = ((A_{control} - A_{sample})/A_{control}) \times 100 \quad ...(1)$$

where $A_{control}$ is the absorbance of the control and A_{sample} is the absorbance of the sample. The mean values were performed from triplicate analysis.

Kinetics Modeling

The rate law explains the dependence of reaction rate on reactant concentration. The change in quality index with time (dc/dt) was describe dusing simple kinetic model as presented in equation (2):

$$dC/dt = \pm kC^n \quad ...(2)$$

where k is reaction rate constant, n is reaction order, t is reaction time (min) and C is GABA concentration (mg/mL) or DPPH radical scavenging activity (%).[22] The negative sign in equation (2) uses for a tested parameter showing degradation, the quality index decreased with time at constant temperature. The positive sign applies for a tested parameter reflecting increase with time that the formation of the product was observed.[23,24]

A kinetic modeling was proposed and interpreted to mathematical equations by deriving the differential equations for reaction in terms of zero–, first– and second–order kinetics. The differential equation was solved through integration and then fitted with experimental resultsby non-linear regression in which the k value of reaction was estimated.[11] The kinetic order of reaction was decided from the best fit line, which showed the highest coefficient of determination (R^2) and the lowest root mean square percent (RMS).[23,25]

Temperature dependence on the rate constant was expressed by Arrhenius model (equation (3)) by plotting lnk against 1/T and activation energy (E_a) was achieved from slope of straight line.[11,22]

$$k = k_0 \exp(-E_a/RT) \quad ...(3)$$

where k is the reaction rate constant, k_0 is the frequency factor or Arrhenius constant, E_a is the activation energy (J/mol),T is absolute temperature (K) and R is the universal gas constant (8.314 J/mol.K).

Half–life time ($t_{1/2}$) is the period needed for 50% of decrease or increase of its initial content. The half–life times were calculated using equations (4) and (5) for first– and second–order reaction kinetics, respective.[26]

$$t_{1/2} = \ln 2 / k \quad ...(4)$$

$$t_{1/2} = 1 / (kC_0) \quad ...(5)$$

where k is rate constant of any order, C_0 is an initial concentration.

The coefficient Q_{10} (temperature coefficient) indicates the effect of change the temperature by 10°C on the reaction rate constant, as in equation (6):[11,12]

$$Q_{10}=(k_2 / k_1)^{(10 / (T_2 - T_1))} \quad ...(6)$$

where k_1 and k_2 are the rate constants of reaction at temperature T_1 and T_2, respectively.

Thermodynamic functions of activation including enthalpy (ΔH) and entropy (ΔS) for changesof GABA and DPPH radical scavenging activity were obtained from Eyring–Polanyi model (equation (7)). The factor $(C^{\theta})^{1-\Delta m}$ is used to acquire the right unit for rate constant of any order.[19] The free activation enthalpy (ΔG) was further calculated as followed equation (8), which directly relate to the activation enthalpy and activation entropy.

$$k = k_B / h_p \; T \exp(-\Delta H + T \cdot \Delta S) / RT) \; (C^{\theta})^{1 - \Delta m} \quad ...(7)$$

$$\Delta G = \Delta H - T\Delta S \quad ...(8)$$

where k_B is Boltzmann's constant (1.381×10^{-23} J/K), h_p is Plank's constant (6.626×10^{-34} J.s), T is absolute temperature (K), R is gas constant (8.314 J/mol.K), ΔG is free activation enthalpy (J/mol), ΔH is activation enthalpy (J/mol), ΔS is activation entropy (J/mol.K), c^{θ} is concentration of GABA (mg/mL) or DPPH radical scavenging activity (%) at the standard state that is at room temperature (30°C) under atmospheric pressure (1 atm)and Δm is the molecularity (first–order reaction kinetic: Δm=1, second–order reaction kinetic: Δm=2).[19]

The Ball model (equation (9)) is applied to calculate the decimal reduction value (D value), which is the time required to reduce a concentration by a factor of 10. The D is correlated to temperature via a Z value. A plotting of log D versus T (°C) is acquired to be a straight line in which the Z value was obtained from slope.[11,18,19] According to first– and second–order reaction, D values were estimated from equations (10) and (11), respectively.[19]

$$D = D_0 \, 10^{-T/Z} \quad ...(9)$$

$$D = 2.303 / k \quad ...(10)$$

$$D = 9 / (C_0 \, k) \quad ...(11)$$

where T is temperature (°C), D is the heating period needed to change the GABA or antioxidant activity by 90% (min), D_0 is Dvalue at temperature of 0°C (min), Z is the temperature required to change the D value by 1 logcycle or a factor of 10 (°C) and k is rate constant of any order.

Model Evaluation

The fitness of the models including zero–, first– and second–order reaction kinetics to experimental data were determined using the coefficient of determination (R^2) and root mean square percent (RMS,%) (equation(12)). The highest R^2 value and the lowest RMS value were accepted as the best fitting to the experimental data.[23,25]

$$RMS,\% = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{P_{obs} - P_{pred}}{P_{obs}}\right)^2} \times 100 \quad ...(12)$$

where n is an observation number, P_{obs} is the observed parametric values and Ppred is the predicted parametric values.

Results and Discussion

Effect of Heat Treatment on GABA

Since GABA is of great importance in GRJM, thus it is reasonable to determine the thermal degradation of GABA in which this information can be applied for the production process. Thermal degradation of GABA in GRJM was studied at 80–121°C (Figure 1). The initial GABA concentration of GRJM was 0.0458 mg/mL. Slight decreases in GABA concentrations were observed throughout the entire 30 min of heating each of 80, 90 and 100°C, while GABA declined significantly during heating at 121°C. Thus, after heating at 80, 90, 100and 121°C at the end of 30 min, GABA decreased to 0.0430, 0.0419, 0.0415 and 0.0313 mg/mL, respectively, which the remaining of GABA in GRJM were 94, 92, 90 and

68%, respectively. These results indicated that GABA was more stable at lower temperature and shorter time. Under thermal treatment,the possible mechanism of GABA degradation is elimination of water molecule and thenformation of the ring closing γ-butyrolactan. Another one mechanism is decomposition by dimerization, which two GABA molecules react and consequently form the different molecular species.[9,27] In accord, Khan *et al*.[9] reported that GABA in *Monascus*–fermented rice solution varied directly with temperature. The GABA residues in *Monascus*–fermented rice solution at different pH values (3.4, 5.4 and 8.0) were 66.4–76.5, 51.9–61.[9] and 14.3–41.0%after heating for 30 min at 80, 100 and 121°C, respectively.

Kinetics Modeling of GABA Degradation

The influence of processing on quality index can be manipulated by kinetic models. Knowledge of kinetics, namely reaction rate constant, kinetic order of reaction and activation energy, is all important in predicting the food quality index during thermal treatment. The degradation of GABA fitted the best with second–order reaction kinetic based on the relatively high R^2 and low RMS(R^2=0.883–0.988, RMS=0.307–5.731%) (Figure 1) as compared to first– (R^2=0.850–0.987, RMS=0.326–6.785%) and zero–order kinetics (R^2=0.813–0.985, RMS=0.347–7.929%) (Table 1). This confirmed that GABA degradation in GRJM in relation to temperature logically fitted second–order kinetic. The second–order kinetic is suitable to describe the dimerization in which the biomolecules combine to form a larger molecule.[19] In case of GABAdegradation pathway, the dimerization reaction may occur under thermal condition.[27] Kinetics parameters of GABA degradation during thermal treatment based on second–order reaction are given in Table 2. The reaction rate constants for GABA loss were in the range of 0.0498–0.4090 min^{-1} and affected by heating temperature. The degradation rate of GABA was increased as the heating temperature increased because the temperature accelerated the rate of degradation. The results indicated that GABA was more stable under lower temperature such as under pasteurization process (80–100°C) as shown by low rate constant. However, this was in contrast to the finding by Khna *et al*.[9] that GABA in *Monascus*–fermented rice solution degraded by first–order reaction, but consistent the result in the present study that the rate constant increased with higher temperature.

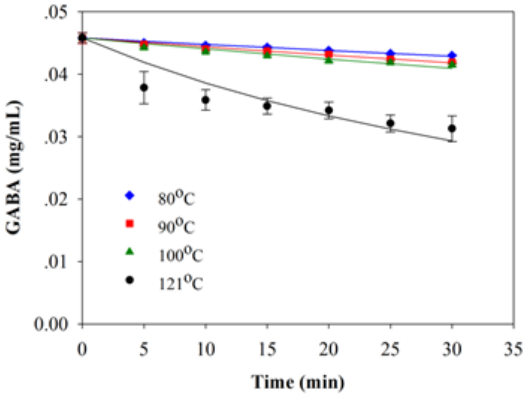

Fig. 1: Second-order kineticplots of γ–aminobutyric acid (GABA) degradation in germinated red jasmine rice milk during heating. Experimental data and simulation are symbol and solid line

Table 1: Reaction order estimation of degradation of γ–aminobutyric acid (GABA) based on the coefficient of determination (R^2) and the root mean square percent (RMS) from plots of zero-, first- and second-order reactions

Temperature (°C)	Zero-order		First-order		Second-order	
	R^2	RMS	R^2	RMS	R^2	RMS
80	0.985	0.347	0.986	0.326	0.987	0.307
90	0.985	0.485	0.987	0.448	0.988	0.415
100	0.941	1.120	0.948	1.043	0.954	0.969
121	0.813	7.929	0.850	6.785	0.883	5.731

Time to 50% degradation of GABA content in GRJM ($t_{1/2}$) within the temperature bounds of this study varied within the range of 438–53 min (Table 2). The increase in temperature caused the decrease in half–life time. Maximum half–life time was 438 min due to the slow rate of GABA degradation at 80°C, confirmation of their relationship. These results were in accordance with Khna*et al*.,[9] who found that the half–life time for GABA degradation in *Monascus*–fermented rice reduced inversely with heating from 80°C to 121°C. For example, half–life time of GABA in *Monascus*–fermented rice solution at pH 3.4 decreased from 231 min to 6.5 min with a temperature increase from 80°C to 121°C. These results indicated degradation of GABA in GRJM was less sensitive to heating than *Monascus*–fermented rice solution.

Table 2: Isothermal kinetic parameters k, $t_{1/2}$, Q_{10} and D values vs temperature for degradation of γ–aminobutyric acid (GABA) and change of DPPH radical scavenging activity (DPPH RSA) in germinated red jasmine rice milk

Reaction	Temperature (°C)	k	$t_{1/2}$ (min)	Q_{10}		D value (min)
				80-90°C	90-100°C	
GABA (second order)	80	0.0498	438	1.40	1.25	3,946
	90	0.0653	314			2,827
	100	0.0871	250			2,256
	121	0.4090	53			480
Increasing in DPPH	80	0.0033	210	1.91	0.90	698
RSA (first order)	90	0.0063	110			366
	100	0.0057	122			404
Decreasing in DPPH	121	0.0149	47	-	-	155
RSA (first order)						

k (reaction rate constant, mL/mg.min for GABA degradation, min^{-1} for change of DPPH RSA), $t_{1/2}$ (half-life time), R^2 (coefficient of determination), RMS (root mean square percent), D value (decimal reduction value)

The Q_{10} values determined for GABA degradation at the temperature ranges of 80-90 and 90-100°C were 1.40 and 1.25, respectively (Table 2). This indicated that the degradation rate of GABA in GRJM was greatly influenced as the temperature increased from 80 to 90°C. On the other hand, the relatively low value of Q_{10} within the temperature of 90-100°C showed that the GABA degradation rate was barely affected forthis temperature range.[28]

Arrhenius Model

Temperature dependence of the rate constants in this study followed Arrhenius relationship as supported by high coefficient of determination (R^2=0.929) (Figure 2A). Within the heat treatment range (80–121°C), the activation energy of GABA degradation in GRJM was 56.92 kJ/mol (Table 3). This is within the reported activation energy ranges (18.19–101.50 kJ/mol) for GABA degradation during heating in *Monascus*–fermented rice solution at pH 3.4 to 8.0 and temperature of 80°C to 121°C.9 Higher activation energy suggested that a small temperature change is required to degrade GABA more rapidly.[26,29] Relative differences in activation energy values may reflect different compositions of sample or reactions during thermal treatment.[30]

Eyring–Polanyi Model

The Eyring–Polanyi model is applied commonly in interpreting temperature dependence of the second–order rate constant.[31] The activation enthalpy (ΔH) and activation entropy (ΔS) were provided by regression analysis of ln ($k.h_p.C^{\theta}/k_B.T$) and the inverse of temperature from the Eyring–Polanyi model using second–order reaction kinetic. We found that Eyring–Polanyi model described well the

temperature dependence of k values (R^2=0.929) (Figure2B). The values of ΔH, ΔS and ΔG for GABA degradation in GRJM under heat treatment range of 80–121°C were 59.61 kJ/mol, –164.12kJ/mol.K and 120.49 kJ/mol, respectively (Table 3). The values of ΔH and ΔS in the present study were within the range demonstrated by Khna*et al*.9, for GABA degradation in *Monascus*–fermented rice solution under the same heating regimes (ΔH=14.91 to 98.56 kJ/mol, ΔS=–24.60 to –233.43 kJ/mol.K). The ΔG presents the difference between reactant and activated state, hence it is positive sign, indicating that the molecules numbers in the activated state is very low when compared to molecules in the non–activated state.[19] Additionally, the positive sign of ΔH describes an endothermic state between the reactant and activated state, which an increasing in deterioration is leaded with the increasing temperature. The relatively high ΔS value implies high significance of this function. The negative sign of ΔS shows the change of disorder after the new molecules were formed in system from reaction of GABA degradation e.g. dimerization.[11,28,32]

Table 3: Thermal kinetic parameters for degradation of γ–aminobutyric acid (GABA) and increasing of DPPH radical scavenging activity (DPPH RSA) in germinated red jasmine rice milk using different models

Reaction	rrhenius model			Eyring-Polanyi model			Ball model		
	k_0	E_a (kJ/mol)	R^2	ΔH (kJ/mol)	ΔS (J/mol.K)	R_2	D_0 (min)	Z(°C)	R^2
GABA	2.7×107	59.62	0.929	59.61	-164.12	0.929	1.8×107	44	0.944
DPPH RSA	112.96	30.31	0.632	30.31	-241.29	0.632	5.5×103	84	0.616

k_0 (Arrhenius constant, mL/mg.min for GABA degradation, min^{-1} for DPPH RSA increasing), E_a (activation energy), R^2 (coefficient of determination), ΔH (activation enthalpy), ΔS (activation entropy), D0 (value of D at temperature of 0°C), Z (the required temperature for change of one $\log_{10}$ D value)

Ball Model

Thermal resistance approach of GABA degradation in term of decimal reduction time (D value) using second–order reaction kinetic was estimated using equation (11).[19] D values varied within the range of 3,946–480 min for heat treatment at 80–121°C (Table 2). D values decreased significantly with heating temperature. This indicated that the time required to decrease GABA content by 90% was shorter at higher temperature. According to Ball model, D values were fitted very well with high value of R^2 (R^2=0.949) (Figure2C). The values of Z and D_0 were 44°C and $1.8×10^7$ min, respectively (Table 3).

Effect of Heat Treatment on Antioxidant Activity

DPPH radical scavenging activity of GRJM was 6.97, 7.10, 8.03 and 8.03% at the initial of heat treatment at 80, 90, 100 and 121°C, respectively. When temperature and time increased from 80°C to 100°C and 0 min to 30 min, respectively, antioxidant activityincreased significantly, in contrast to declining at 121°C (Figure 3). After heating at 80, 90, 100 and 121°C, these values were 15.67, 23.44, 21.33 and 5.04%, respectively. Increases in GRJM antioxidant activity relative to initial values after heating were 125% (80°C), 230% (90°C) and 164% (100°C). In marked contrast, antioxidant activity in GRJM declined to 37% of its initial value after heating to 121°C. In addition, it is obvious that GABA decreased (under 80–121°C), while the antioxidant activity increased (under 80–100°C). This demonstrated that GABA was not correlated with sample antioxidant activity. The improvement of antioxidant activity may result from liberating free fraction phenolic compounds or low molecular weight phenolic compounds from bound phenolic compounds by heat treatment. In addition, the new antioxidants including Maillard reaction products may be formed during heating.[10,12,16] On the other hand, the loss of antioxidantssuch as anthocyanin, heat labile compounds as well as the synthesis of compounds exhibiting pro–oxidant activity may

cause a decline in antioxidant activity under heating at high temperature (121°C).[10] This result suggested that the processing GRJM by heating at temperature ranges of 80–100°C improved its antioxidant capacity. This result was in conformance with previous studies, which indicated the enhancement of antioxidant activity in fruits and vegetables during heat treatment.[10,13,16,17] Sharma *et al*.[10] reported that the antioxidant activities (DPPH and FRAP values) of six onion varieties increased at higher temperature from 80°C to 120°C, but the antioxidant activities for all varieties were less at 150°C as compared to 120°C. Moreover, Turkmen *et al*.[33] reported that the increase of antioxidant activity versus brown pigment formation in honey during heating at 50–70°C showed a strong relationship, confirming that Maillard reaction products acted as antioxidants.

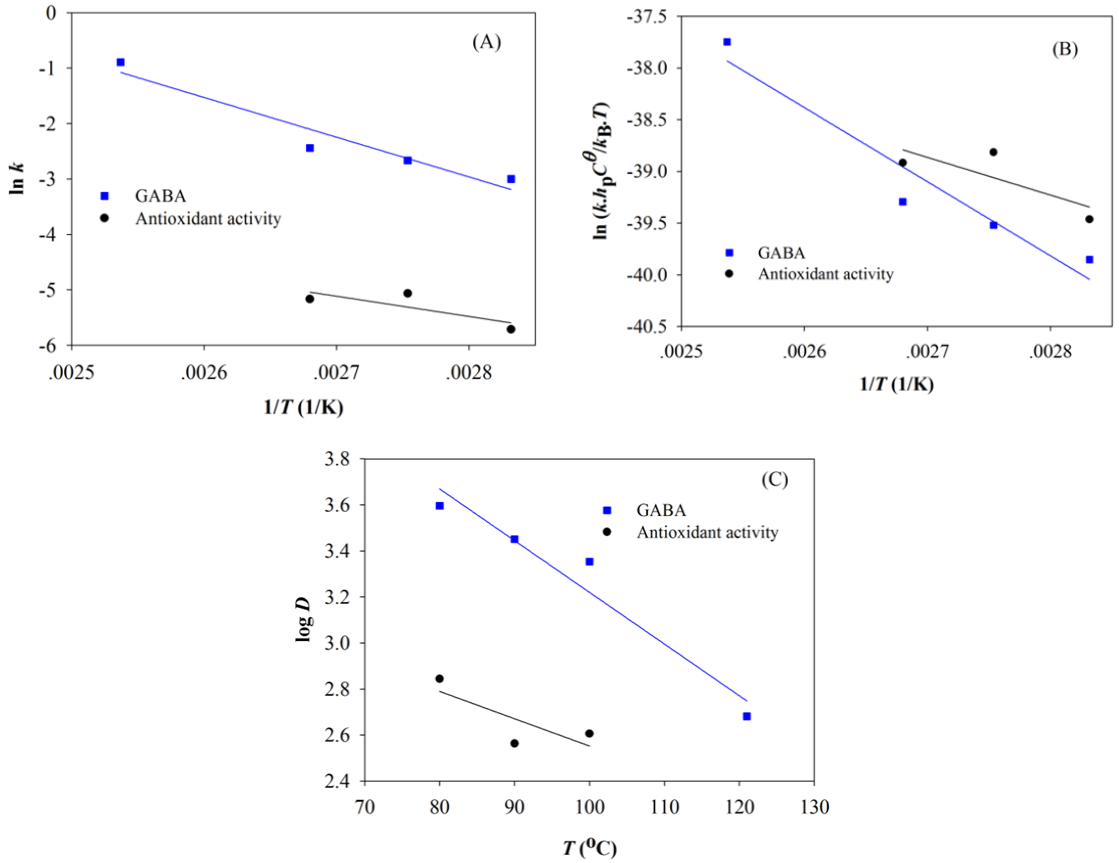

Fig. 2: Effect of the heating temperature on degradation of γ–aminobutyric acid (GABA) and increasing of DPPH radical scavenging activity following Arrhenius (A), Eyring–Polanyi (B) and Ball (C) models (lines) from germinated red jasmine rice milk during heating

Kinetics Modeling of Change of Antioxidant Activity

Regarding the thermal kinetics of antioxidant activity, DPPH radical scavenging activity of GRJM increased from 80–100°C, but decreased at 121°C. The chemical reaction pathways differed suggesting different kinetics models need be applied. Non–linear regression analysis demonstrated that the increasing of antioxidant activity in GRJM (under 80–100°C) was described adequately by zero– (R^2=0.839–0.996, RMS=3.774–13.918%), first– (R^2=0.851–0.996, RMS=4.294–13.153%) and second–order reaction kinetics (R^2=0.863–0.994, RMS=5.036–12.405%)(Table 4). However, the first–order reactionwas often reported for reactions in foods.[19] In the present study, first–order reaction better described kinetic parameters such as D–values than either of the other orders of reactions.

The kinetics data of increasing of antioxidant activity in GRJM during heating at 80–100°C according to the first–order reactionshows in Table 2. The highest reaction rate constant, k, for increasingof antioxidant activity in GRJM was observed at 90°C, followed by 100°C and 80°C, respectively. This can be explained that the rate of increasingof antioxidant activity under 100°C deteriorated at interval of 25–30 min resulting in lower value of the k at 100°C as compared to 90°C (Figure 3). The increase in antioxidant activity has been assessed by previous studies using the zero–, first– and second–order kinetics due to the different reactions. Turkmen *et al*.[33] reported that the increasingof DPPH inhibition in honey indicated different models according to the heating temperatures following second–, first– and zero–order reaction kinetics at 50, 60 and 70°C, respectively. As well, Molaveisi *et al*.[34] stated that the increasing of DPPH inhibitionin Iranian jujube honey with heating time followed second–, first– and zero–order reaction kinetics at 45, 55 and 65°C, respectively. Besides, Suh *et al*.[35] reported that the first– and zero–order kinetic models were suitable for prediction the increasing of antiradical capacity of mulberry fruit extract during treatment period at 80–100°C with high R^2 value.

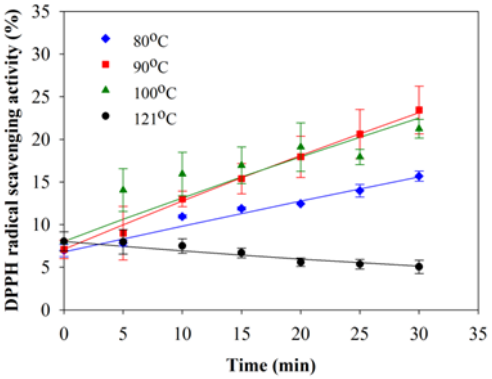

Fig. 3: First-order kineticplots of the change of DPPH radical scavenging activity in germinated red jasmine rice milk during heating. Experimental data and simulation are symbol and solid line

Table 4: Reaction order estimation of change of DPPH radical scavenging activity (DPPH RSA) based on the coefficient of determination (R^2) and the root mean square percent (RMS) from plots of zero-, first- and second-order reactions

Reaction	Temperature	Zero-order		First-order		Second-order	
	(°C)	R^2	RMS	R^2	RMS	R^2	RMS
Increasing in DPPH RSA	80	0.967	5.299	0.968	5.145	0.970	5.036
	90	0.996	3.774	0.996	4.294	0.994	5.067
	100	0.839	13.918	0.851	13.153	0.863	12.405
Decreasing in DPPH RSA	121	0.944	4.993	0.952	4.478	0.928	5.819

Kinetic degradation of DPPH radical scavenging activity inGRJM at 121°C was described well by first–order reaction kinetic with high R^2 and low RMS values (R^2=0.952, RMS=4.478%) (Table 4).The rate constant for degradation of DPPH radical scavenging activity was 0.0149 min^{-1} (Table 2). This result was in agreement with many earlier studies on the first–order reaction kinetic for thermal degradation of antioxidative capacity including banana–pumpkin puree,[11] ground apples,[14] kiwifruit puree,[15], plum[30] and blackberry.[36]

The highest half–life time for increasing of DPPH radical scavenging activity inGRJM was 210 min at 80°C, but decreasedsignificantly to 110 min at 90°C, showing the slow rate of rising of antioxidant activity at 80°C. In addition, the half–life time of thermal degradation of DPPH radical scavenging activity inGRJM under heating at 121°C was approximately 47 min (Table 2).In addition, the highest Q_{10} value was obtained for the heating temperature range of 80-90°C. Thus, as the temperature rose from 80 to 90°C, the increasing rate of DPPH radical scavenging activity of GRJM was influenced more than that of the temperature range of 90–100°C (Table 2).

Arrhenius Model

Activation energy for increasing of DPPH radical scavenging activity at 80–100°C of GRJM from Arrhenius plot was 30.31 kJ/mol (R^2=0.632) (Table 3 and Figure 2A). The low value of R^2 of the Arrhenius model was obtained due to the unusual relationship between k values and temperatures (80–100°C) (Table 3). Similar to this result, the activation energy value of rising of DPPH radical scavenging activity in beetroot during blanching at 70–90°C has been reported approximately 22.70 kJ/mol.[13] The relatively high activation energy of increasing of antioxidant activity in GRJM implied that the increasing of antioxidant activity in GRJM was more susceptible to change in the temperature when compared to increasing of antioxidant activity in beetroot.[26,29]

Eyring–Polanyi Model

According to Eyring–Polanyi model, the ΔH and ΔS were determined by plotting $\ln(k.h_p/k_{B\cdot T})$ versus 1/T using first–order reaction (Figure 2B).[19] Over the temperature range studied (80–100°C), the values of ΔH, ΔS and ΔG for increasing of antioxidant activity in GRJM were 30.31 kJ/mol, –241.29 J/mol.K and 117.93 kJ/mol, respectively (Table 3). The positive sign of ΔH indicates the leading of antioxidant activity with increasing temperature. The negative sign of ΔS implies that anincrease in order resultedfrom forming an activated complex.[28] The increase of antioxidant activity in GRJM presented higher value of ΔH than that in beetroot (ΔH=19.83 kJ/mol),[13] indicating that the k values for increase of antioxidant activity in GRJM was more affected by temperature.[11]

Ball Model

According to the first–order kinetic, the heating period needed to increase DPPH radical scavenging activity by 90% from its initial D value were varied within the range of 698-404 min at 80-100°C, while that to reduce antioxidant activity by 90% at 121°C was 155 min(Table 2). The D values to increase antioxidant activity in GRJM (698–404 min) were higher than those in beetroot from 70–90°C (282–181 min).[13] This suggested that the heating time needed to increase antioxidant activity in beetroot during heating was shorter as compared to GRJM. From Ball model (Figure 3C), Z and D_0 were 84°C and 5.5×10^3 min, respectively to increase antioxidant activity in GRJM from 80–100°C (Table 3).

Validation of Kinetics Modeling

To validate the models in estimation of experimental data, the k values for degradation of GABA (under 80–121°C) and increasing of antioxidant activity (under 80–100°C) were simulated by Arrhenius, Eyring–Polanyi and Ball models. The GABA content and antioxidant activity at any time of heating were calculated using second– and first–order reaction, respectively. The results showed that the fitting of Arrhenius, Eyring–Polanyi and Ball models with experimental results of GABA content gave high R^2 within the ranges of 0.874–0.998, 0.877–0.988 and 0.876–0.988, respectively as well as low RMS within the ranges of 0.459–6.683, 0.423–6.113 and 0.434–6.284, respectively. In addition, Arrhenius, Eyring–Polanyi and Ball models also adequately described experimental data for antioxidant activity with R^2 intervals of 0.853–0.996, 0.853–0.996 and 0.853–0.966, respectively and RMS intervals of 6.382–13.770, 5.718–14.135 and 7.043–13.868, respectively.

Conclusion

The present study showed negative correlation between GABA and DPPH radical scavenging activity. GABA degradation in GRJM during heat at 80–121°C was best explained by second–order reaction kinetic. The increasing of antioxidant activity in GRJM during heat at 80–100°C followed first–order kinetic as well as a decrease of antioxidant activity at 121°C. The results of the kinetic parameters indicated that GABA and antioxidant activity of GRJM were influenced by heating temperature. Maximum retention of GABA were 94% at 80°C for 30 min, while the maximum increase of antioxidant activity was 230% after heating at 90°C for 30 min. Variation in rate constant for degradation of GABA and increasing of antioxidant activity in accordance with temperature followed Arrhenius, Eyring–Polanyi and Ball relationship. This study will be of significant help in prediction and comprehending of changes of GABA, a critical compound, and antioxidant capacity in GRJM for manufacturing in industrial scale.

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Conflict of Interest
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