

Thermal Stability of Anisoyl Kaempferol Glycosides in Jack Bean (*Canavalia ensiformis* (L.) DC) and Their Effect on α -Glucosidase Inhibition

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ABSTRACT: Kaempferol glycosides are functional components of jack bean. The chemical stability of kaempferol glycosides under simulated food processing conditions was evaluated in this study by subjecting the methanol extract and each compound to heat treatment. During the heat treatment, rearrangement of the anisoyl group on the rhamnose moiety of the kaempferol glycoside was observed, followed by hydrolysis upon long-term heat treatment. One of the two regioisomers produced under heating conditions showed higher α -glucosidase inhibitory activity than the dominant anisoyl kaempferol glycoside. This rearrangement reaction was also observed upon the heat treatment of methyl-3-O-anisoyl-rhamnose, with the rearrangement from the 3-position to the 2-position occurring preferentially. The approach adopted in this study can be used to design appropriate food processing conditions, which, in turn, will increase the functional value of foods.

KEYWORDS: food processing, thermal stability, kaempferol glycosides, jack bean

INTRODUCTION

Secondary metabolites in plants are widely known to be active compounds that are beneficial to human health. Flavonols, one such class of secondary metabolites, exhibit significant biological activity. Many types of flavonols with diverse structures have been reported so far. In addition, structure–activity relationship studies of flavonols have been actively conducted, which reported that the presence of substituents can enhance or reduce some biological activities. Flavonols are thermally unstable.^{1–3} Plant-based foods, such as vegetables, cereals, and legumes, are generally processed before consumption. Although food processing is aimed to increase digestibility, it affects the bioactive compounds contained therein.^{4–6} For instance, thermal processing such as roasting, frying, and boiling can degrade flavonol glycosides, and this shall be the focus of this study.^{7–9}

Jack bean (*Canavalia ensiformis* (L.) DC), a legume consumed in some countries, has been rarely processed into food products. Several studies have shown that jack bean has high flavonoid and protein contents.^{10–12} In our previous study, kaempferol glycosides were isolated from this bean.¹³ There are two types of dominant kaempferol glycosides, which are distinguished based on the presence or absence of an anisoyl group on the rhamnose moiety. Anisoyl kaempferol glycosides showed better inhibitory activity against α -glucosidase than kaempferol glycosides without an anisoyl group.¹³ Therefore, jack bean can be used as a functional food material. However, jack bean has a very hard texture and must be processed, for instance, by boiling, to soften the texture. To be used as a functional food material, the stability of these compounds during heating must be examined. This study aimed to evaluate the stability of kaempferol glycosides, with or without an anisoyl group, during heating.

MATERIALS AND METHODS

Plant Materials. Jack beans (*C. ensiformis* (L.) DC) were purchased from a local farmer in Temanggung, Central Java, Indonesia, in 2017. The broken, molded, sprouted, and damaged beans were first separated. The beans were further peeled, ground, and sieved through a 100-mesh sieve to prepare jack bean flour. The samples were stored at $-30\text{ }^{\circ}\text{C}$ before analysis.

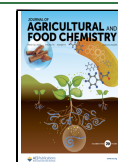
Extraction. Jack bean flour was extracted as described in our previous study.¹³ Jack bean flour (1000 g) was removed from the lipid using hexane before extraction. The flour was then extracted with methanol (1:5, three times) at room temperature for 2 h, filtered, and concentrated under reduced pressure at $30\text{ }^{\circ}\text{C}$ to obtain the crude methanol extract (yield: 59.2 g). The crude extract was stored at $-30\text{ }^{\circ}\text{C}$ before analysis.

Kaempferol 3-O- α -L-rhamnopyranosyl (1 $\rightarrow$ 2) [α -L-rhamnopyranosyl (1 $\rightarrow$ 6)]- β -D-glucopyranoside-7-O- α -L-rhamnopyranoside (2) and kaempferol 3-O- α -L-rhamnopyranosyl (1 $\rightarrow$ 6)]- β -D-glucopyranosyl (1 $\rightarrow$ 2)]- β -D-galactopyranosyl-7-O-[3-O-*o*-anisoyl]- α -L-rhamnopyranoside (4a) were isolated from jack bean as described in our previous study.¹³ The crude methanol extract was suspended in water (200 mL) and chromatographed on a Diaion HP-20SS (Mitsubishi Chemical Corporation, Tokyo, Japan) column. Elution was performed using a water–methanol mixture, with the methanol content increasing gradually (0, 20, 50, 80, and 100 vol %). Compound 2 was isolated from the fraction with 50% methanol by silica gel open-column chromatography using a chloroform–methanol–water (14:6:1 and 13:7:1) mixture. The yield of compound 2 was 2.76 mg. Compounds 4a–c were isolated from the fraction with 80%

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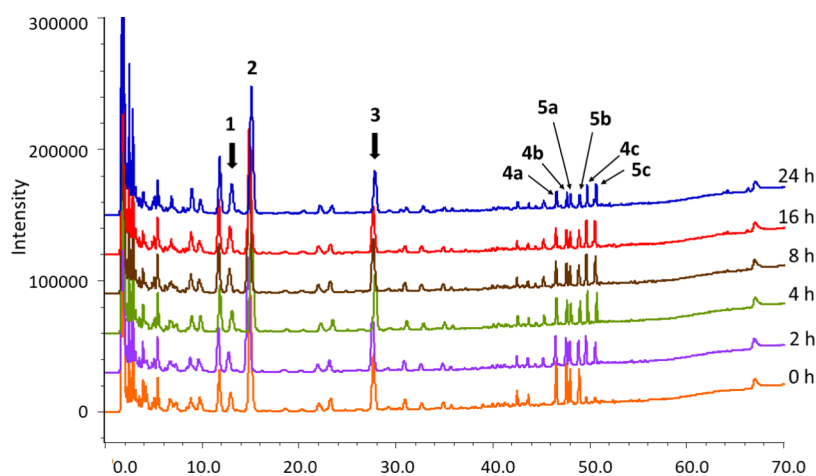


Figure 1. Chromatogram of the crude extract upon heating at 95 °C for 24 h. The peak numbers indicate the compound number.

methanol and subjected to preparative high-performance liquid chromatography (HPLC) on a chromatograph equipped with a Jasco PU2089 intelligent pump, a Jasco UV-2075 detector (Tokyo, Japan), and a Shimadzu CTO-10ACVP column oven (Kyoto, Japan). The Cosmosil 5C18-MS-II column (10 mm I.D. × 250 mm, particle size 5 μ m) used for separation was maintained at 35 °C. Elution was performed at a flow rate of 5.0 mL/min using an 80:20 water–acetonitrile mixture containing 0.5% formic acid. Signals from the analyte were detected at 254 nm. The yields of compounds **4a–c** were 0.83, 0.65, and 0.30 mg, respectively.¹³

Heat Treatment. The crude methanol extract (75 mg) was dissolved in 2 mL of deionized water. This sample solution (250 μ L) was transferred to a 1.5 mL sealed microtube and heated at 95 °C using a dry thermo unit (DTU-1BN Taitec, Japan) for 0, 2, 4, 8, 16, and 24 h.

Isolated compounds **2**, **4a**, and synthetic methyl-3-O-anisoyl- α -L-rhamnopyranoside (**7i**) were dissolved in water (0.1 mg/250 μ L) and heated at 95 °C using the dry thermo unit for 0, 2, 5, 10, 30, 60, 120, and 240 min.

HPLC. Five microliters of the sample was injected into a reverse-phase HPLC-PDA system equipped with a Jasco PU2089 intelligent pump, a Jasco MD-2010 plus detector, and a Jasco CO-2065 Plus column oven (Tokyo, Japan). Chromatographic separation was performed on a reversed-phase column (Cosmosil 5C18-MS-II, 4.6 mm I.D. × 150 mm; particle size, 5 μ m) maintained at a temperature of 35 °C. Signals were detected at 254 nm. The mobile phases for the crude methanol extract were 0.5% formic acid (FUJIFILM Wako Pure Chemical, Japan) in water (A) and acetonitrile (B) (Kanto Chemical, Osaka, Japan). Gradient elution was conducted for 70 min as follows: 10% B for 10 min, 15% B till 30 min, 25% B till 45 min, 35% B till 55 min, 45% B till 60 min, and 55% B till 70 min. Compounds **2**, **4a**, and **7i** were analyzed under isocratic conditions. The mobile phase was 88:12, 77:23, and 75:25 water–acetonitrile mixtures containing 0.5% formic acid for **2**, **4a**, and **7i**, respectively. The flow rate of the mobile phase was set to 1 mL/min.

Ultrahigh-Performance Liquid Chromatography–Time-of-Flight Mass Spectrometry. The compounds were analyzed on a UPLC system coupled to a quadrupole time-of-flight mass spectrometer (QTOF-MS; Waters Xevo G2 QTof, Waters, Milford, MA) operated in the electrospray ionization (ESI) mode at a mass resolution of 20 000 and controlled by MassLynx 4.1 software. Chromatographic separation of compounds **4a** and **7i** was performed on an Acquity UPLC BEH C18 column (2.1 mm I.D. × 100 mm; particle size 1.7 μ m, Waters) at a temperature of 35 °C. The mobile phases were 1% formic acid in water (A) and acetonitrile (B), and samples were eluted isocratically using 20% B for 20 min. The sample (1 μ L) was injected using an autosampler. The mass spectrometer was calibrated with 0.5 mM sodium formate. Leucine enkephalin (2 μ g/mL, m/z 5562 771 in the positive mode) was used as a lock spray at a flow rate of 10 μ L/min. The collision energy was set to 6 V. The

source parameters were as follows: capillary voltage, 2.5 kV; sampling cone voltage, 30 V; extraction cone voltage, 4 V, 25–30 V for MS/MS; source temperature, 150 °C; desolvation temperature, 500 °C; desolvation gas flow rate, 1000 L/h; and cone gas flow rate, 50 L/h.

In Vitro α -Glucosidase Inhibitory Activity. The α -glucosidase inhibitory activity was assayed *in vitro* using a 96-well plate, as previously reported.¹⁴ Compound **4a**, **4b**, **4c**, or acarbose (1 mg each, acarbose is the positive control) was dissolved in 200 μ L of dimethyl sulfoxide (DMSO), and 800 μ L of phosphate buffer (50 mM, pH 6.9) was added. The sample solution (50 μ L/well) was mixed with α -glucosidase (0.5 U/mL; 20 μ L/well; diluted in phosphate buffer) from *Saccharomyces cerevisiae* (Type I, Sigma-Aldrich, St. Louis, MO). After preincubation at 37 °C for 15 min, the assay was initiated by adding 4-nitrophenyl- α -D-glucopyranoside (PNPG) (9 mg/mL; 50 μ L/well; diluted in phosphate buffer) as a substrate. The mixture was then incubated at 37 °C for 15 min. The reaction was stopped by adding Na₂CO₃ (100 mM; 100 μ L/well; diluted in phosphate buffer). The absorbance of the released *p*-nitrophenol (Abs_{sample}) was measured at 415 nm using a Multiplate Reader Spark 10M (Tecan Group Ltd., Switzerland). A solution of 20% DMSO in phosphate buffer was used as a control (Abs_{control}), and each experiment was performed in triplicate. The results, expressed as percent inhibition, were obtained using the formula

$$\text{inhibitory activity (\%)} = (1 - Abs_{\text{sample}}/Abs_{\text{control}}) \times 100\%$$

Using Past 4.0 software (Oslo, Norway),¹⁵ a statistical analysis was performed based on the analysis of variance and Tukey's honestly significant difference (HSD) post hoc test carried out at a significance level of $p < 0.05$ to determine the differences between the samples.

Synthesis of Methyl-L-rhamnopyranoside (6**).** Compound **6** was synthesized as described by Milhomme et al., with some modifications.¹⁶ L-Rhamnose (0.5 g) was dissolved in super dehydrated methanol (7.0 mL, Wako, Japan), and acetyl chloride (4.3 mL, 60.8 mmol, Wako, Japan) was added to the mixture at −10 °C. The mixture was stirred for 12 h at room temperature. The mixture was added to excess sodium bicarbonate, and the solvent was evaporated *in vacuo*. The crude product was purified by silica gel column chromatography (dichloromethane/methanol = 9:1). Compound **6** was obtained in 97.5% yield. NMR spectra were recorded on a 600 MHz JEOL ECA 600 spectrometer (Tokyo, Japan). The chemical structure of compound **6** was identified by comparison with the literature data.¹⁶

Synthesis of Methyl-3-O-anisoyl- α -L-rhamnopyranoside (7i**).** Compound **7i** was synthesized as described by Lv et al., with some modifications.¹⁷ Methyl-L-rhamnopyranoside (**6**, 0.1 mmol, 71.2 mg) in dry acetonitrile (0.5 mL) was reacted with K₂CO₃ (105.2 mg, 1.9 equiv) and 2-methoxybenzoyl chloride (72 μ L, 1.5 equiv). FeCl₃ (6.4 mg, 0.1 equiv) and 4,4,4-trifluoro-1-phenyl-1,3-butanedione (17.6 mg, 0.2 equiv) were used as catalysts. The reaction was carried out at

room temperature for 2 h with stirring, and the reaction mixture was purified directly by open-column chromatography (ethyl acetate/hexane = 1:2).

Compound **7i** was purified by preparative HPLC (Jasco, Tokyo, Japan). The components were separated on an Inertsil Prep-ODS column (10.0 mm I.D. $\times$ 250 mm; particle size, 5 μ m) at 35 $^{\circ}$ C. The mobile phase was a 75:25 water–acetonitrile mixture containing 0.5% formic acid. Isocratic elution was performed at a flow rate of 5 mL/min, and compound **7i** was obtained in 95% yield. The NMR data are given in the Supporting Information (Figures S7 and S8).

RESULTS AND DISCUSSION

The crude methanol extract of jack bean was dissolved in water and heated at 95 $^{\circ}$ C. The reaction mixtures were monitored by HPLC (Figure 1). Five kaempferol derivatives were detected in the crude methanol extract, and they were identified to be kaempferol glycosides without (compounds **1–3**) or with (compounds **4a** and **5a**) an anisoyl group, based on liquid chromatography–mass spectrometry (LC–MS) analysis and our previous report.¹³ Compounds **4bc** and **5bc** were identified as kaempferol glycosides with 2'' or 4''-*O*-anisoyl, based on LC–MS/MS analysis (Table 1 and Figure S1). The chemical structures of the compounds are shown in Figure S2.

Table 1. Chemical Structures of Kaempferol Glycosides

com- pound	retention time (min)	M.W.	R ¹	R ²
1	11.8	902	rhamnose	galactose, glucose, rhamnose
2	17.5	886	rhamnose	rhamnose, glucose, rhamnose
3	27.8	740		rhamnose, glucose, rhamnose
4 a	46.5	1036	3''- <i>O</i> -ani- rhamnose	galactose, glucose, rhamnose
b	47.6		2''/4''- <i>O</i> -ani- rhamnose	galactose, glucose, rhamnose
c	49.7			galactose, glucose, rhamnose
5 a	47.9	1020	3''- <i>O</i> -ani- rhamnose	rhamnose, glucose, rhamnose
b	48.8		2''/4''- <i>O</i> -ani- rhamnose	rhamnose, glucose, rhamnose
c	50.5			rhamnose, glucose, rhamnose

The temporal evolution of the major kaempferol glycosides based on the HPLC peak area is shown in Figure 2. The contents of compounds **1** and **2**, which have no anisoyl groups, gradually increased with increasing heating time and became 1.4-fold and 1.1-fold, respectively. In contrast, the content of compound **3** decreased with increasing heating time. The contents of compounds **4a**, **4b**, **5a**, and **5b**, which have an anisoyl group, decreased to about 70% within 2 h. Interestingly, the contents of **4c** and **5c**, which were initially low, increased significantly at 2 h. The contents further increased to approximately 5-fold at 4 h and decreased thereafter. These results suggest that intramolecular rearrangement or hydrolysis of the anisoyl group occurs during the heat treatment.

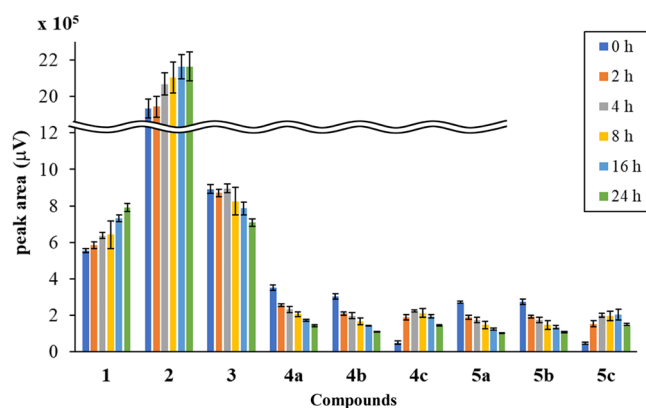


Figure 2. Temporal evolution of the major kaempferol glycosides in the methanol extract of jack bean during heating at 95 $^{\circ}$ C for 24 h. * n = 3; different letters in a sample indicate significant difference (p < 0.05, Tukey's HSD post hoc test).

Compounds **1** and **2** were evaluated for their thermal stability (Figures S3 and S4). The data showed that heating at 95 $^{\circ}$ C for 60 min retarded the degradation of the two compounds. Upon heat treatment for 240 min, only $\sim$ 10% reduction of these compounds was observed. Compound **3** is assumed to be generated from compound **2** upon hydrolysis of the sugar moiety at the 7-position. However, compound **3** was not detected (Figure S4). This is because the glycosidic bond is stronger than the ester bond. Hydrolysis of glycoside can be initiated by the addition of an acid catalyst or by an enzymatic reaction.^{18,19} Thus, these compounds are highly stable compared to kaempferol glycosides with an anisoyl group.^{8,20}

Next, compound **4a** was subjected to heat treatment. During the heat treatment of the methanol extract described above, compound **4a** decreased significantly at 4 h. Therefore, an aqueous solution of compound **4a** was heated at 95 $^{\circ}$ C for up to 4 h and the reaction was monitored by HPLC (Figures 3 and S4). The peak area of compound **4a** decreased, followed by an increase in the peak areas of compounds **4b** and **4c**. The peak area of compound **4b** increased up to 30 min and gradually decreased thereafter. The peak area of compound **4c** increased slowly compared to that of **4b**. This suggested that compound **4a** was converted to **4b** and **4c**.

LC–MS analysis was performed on the heated samples at each treatment time. Compound **1** with m/z 903 [$M + H$]⁺ was detected after 60 min of heating (Figure S5), indicating that the anisoyl group was removed from the compound to form nonanisoyl kaempferol glycosides. On the other hand, compounds **4b** and **4c** were observed earlier than compound **1** during the heat treatment. This result suggests that the rearrangement reaction was more facile than the hydrolysis of the anisoyl group. In addition, as described above, an increase in the content of compound **1** was observed upon heating the aqueous solution of the methanol extract (Figure 3). This is because compound **1** was produced by the hydrolysis of compound **4a** under heating conditions. In contrast, a decrease in the content of compound **3** was observed (Figure 1), probably because an anisoyl derivative with the same glycoside structure was not present in the methanol extract.

Heat Treatment of the Anisoyl rhamnose Derivative.

As described above, there is a possibility of the intramolecular rearrangement of the anisoyl group during the heat treatment of **4a**. However, the structure determination of each compound was difficult because of the low concentration. Hence, methyl-

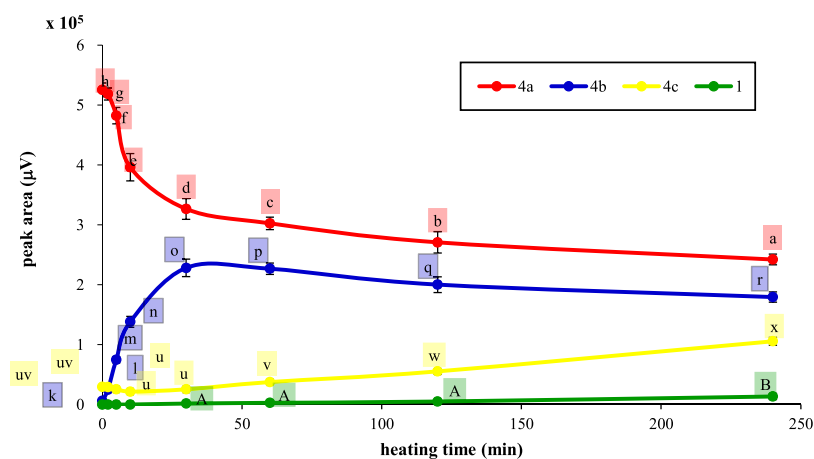


Figure 3. Change in the peak areas of compounds **4a**, **4b**, and **4c** during heating at 95 °C for 4 h. * $n = 3$; different letters in a sample indicate significant difference ($p < 0.05$, Tukey's HSD post hoc test).

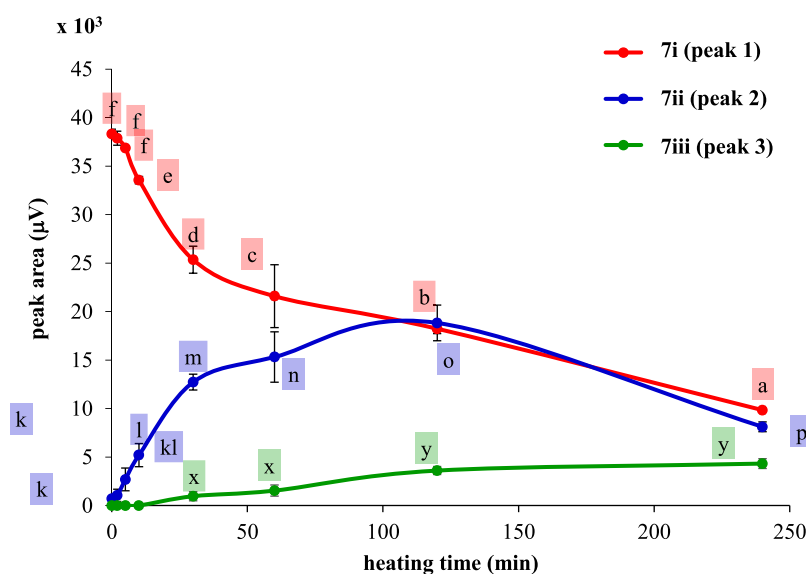


Figure 4. Changes in the peak area of compounds **7i**, **7ii**, and **7iii** during heating at 95 °C for 4 h. * $n = 3$; different letters in a sample indicate significant difference ($p < 0.05$, Tukey's HSD post hoc test).

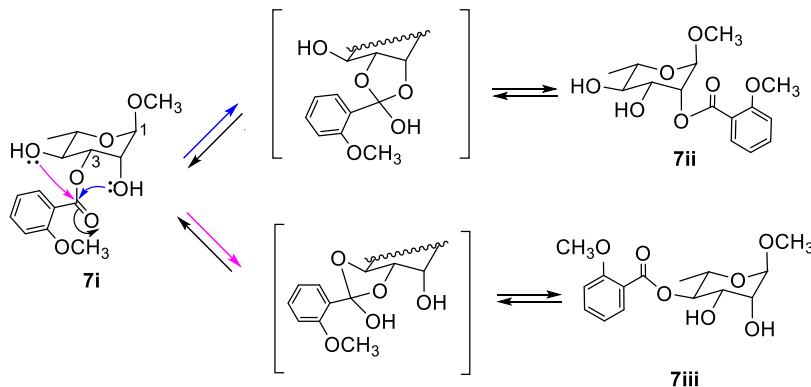


Figure 5. Proposed rearrangement mechanism of the anisoyl group.

3-*O*-anisoyl-rhamnose (**7i**), a sugar with an anisoyl group, was synthesized as a model compound, and it was investigated whether the rearrangement reaction was caused by heating. Aqueous solutions of **7i** were heated at 95 °C for up to 4 h; these are same as the heat treatment conditions of **4a**. The reaction was monitored by HPLC.

The peak area of compound **7i** (peak 1) decreased, followed by an increase in the area of peak 2 (Figure S6A). The area of peak 2 increased up to 120 min and decreased thereafter. Peak 3 was observed 30 min after the initiation of the heat treatment, and the peak intensity slightly increased up to 240 min (Figures 4 and S6A). This result is in good agreement

with the behavior of compound **4a** under heating conditions. According to the LC-MS analysis, molecular ion peaks of peaks 2 and 3 were observed at m/z 335 $[M + Na]^+$, suggesting that they were isomers. Isolation and NMR analysis were performed to determine the chemical structures. Based on the 1H NMR and H–H correlation spectroscopy (H-H COSY) data, peaks 2 and 3 were determined to be methyl-2-*O*-anisoyl-rhamnose (**7ii**) and methyl-4-*O*-anisoyl rhamnose (**7iii**), respectively (Figures S9–S12). The rearrangement reaction of the acyl group in the sugar moiety under acidic and basic conditions is well known. It occurs not only upon acid and base treatment but also under heating conditions.²¹ This rearrangement reaction proceeds through a cyclic orthoester intermediate (Figure 5).²² The yield of **7ii** was higher than that of **7iii**, and **7ii** was produced much early in the course of the reaction (Figure 4). This is because the rearrangement from the 3-position to the 2-position proceeds easily due to the *cis*-configuration. In addition, the total area of peaks 1–3 decreased at 240 min. On the other hand, *o*-anisic acid, which is the hydrolysis product of **7i**, was detected in the sample heated for 240 min (Figure S6B). This suggested that the anisoyl group was hydrolyzed upon prolonged heating.

In Vitro α -Glucosidase Inhibitory Activity of **4a and Its Isomer.** In our previous study, kaempferol glycosides with an anisoyl group (**4a** and **5a**) showed higher α -glucosidase inhibitory activity than those without an anisoyl group.¹³ Because **4a** showed the highest inhibitory activity, the α -glucosidase inhibitory activity of **4a** and its isomers **4b** and **4c** was examined. It was found that **4b** and **4c**, which underwent acyl rearrangement, also exhibited higher inhibitory activity than acarbose, which was used as a positive control (Table 2). This suggested that the heat-induced rearrangement of the anisoyl group in compound **4a** did not decrease its α -glucosidase inhibitory activity.

Table 2. α -Glucosidase Inhibitory Activity of **4a and Its Isomers**

compound ^a	inhibition activity (%) ^b
4a	77.23 $\pm$ 1.81 ^b
4b	73.70 $\pm$ 2.53 ^b
4c	99.07 $\pm$ 0.27 ^b
acarbose (positive control)	54.8 $\pm$ 0.79 ^a

^aInhibitory activity was detected at a sample concentration of 1 mg/mL. ^bValues expressed as mean $\pm$ standard deviation (SD) ($n = 3$). Values followed by different letters indicate statistically significant differences at $p < 0.05$ (Tukey's HSD post hoc test).

The inhibitory activity of compound **4c** was higher than that of **4a**. However, isomerization to **4c** was significantly slow (Figure 3), and thus, it took a long time for this compound to accumulate. The prolonged heat treatment caused hydrolysis of the anisoyl group to generate **1** (Figure S5), thus exhibiting low inhibitory activity.¹³ This suggests that prolonged heating should be avoided to retain the α -glucosidase inhibitory activity of the processed product.

Kaempferol glycoside is a dominant flavonoid in jack bean and exhibits α -glucosidase inhibitory activity. Polyphenols are unstable under food processing conditions, such as heating, and undergo structural changes. Moreover, the chemical structure of bioactive compounds affects their bioactivity. Therefore, we focused on the chemical changes in kaempferol glycosides of jack bean upon heat treatment, a common food

processing condition. The kaempferol glycoside contents increased or decreased with increasing heating time. In the anisoyl kaempferol glycosides, the rearrangement reaction of the anisoyl group on the rhamnose moiety occurred, following which the anisoyl group was hydrolyzed upon further prolonged heating. One of the regioisomers produced under heating conditions exhibited higher α -glucosidase inhibitory activity than the dominant anisoyl kaempferol glycoside. However, prolonged heating caused hydrolysis of the anisoyl group, resulting in a decreased inhibitory activity. Considering the yield of each regioisomer and the hydrolysis reaction rate, this compound is a potential antidiabetic agent when subjected to short-term heat treatment.

To optimize food processing conditions for preventing chemical changes and for accurately evaluating the functional properties of the food, detailed information on the chemical structures of functional components, such as that present in this study, is useful. Because stability and chemical structure are specific to a compound, a further detailed study of the dominant functional components of each food material should be conducted.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jafc.2c00097>.

Mass spectra and chemical structure of the compounds in the sample; change in content of compounds under heating condition; HPLC chromatogram of the heat-treated compounds; and 1H NMR and COSY data of synthetic compounds (PDF)

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Notes

The authors declare no competing financial interest.

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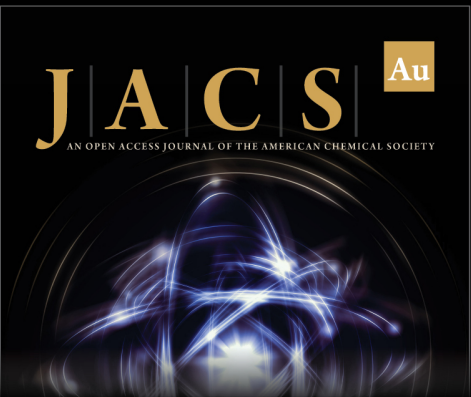
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ABBREVIATIONS USED

UPLC, ultraperformance liquid chromatography; HPLC, high-performance liquid chromatography; QTOF-MS, quadrupole time-of-flight mass spectrometer; NMR, nuclear magnetic resonance; COSY, correlation spectroscopy; LC-MS, liquid chromatography-mass spectrometry; ESI, electrospray ionization

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