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Phenolic glycosides from *Kaempferia parviflora*

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ABSTRACT

Three phenolic glycosides were isolated together with two known flavonol glycosides from the H_2O-soluble fraction of rhizomes of *Kaempferia parviflora*. Their structures were determined to be *rel*-(5a*S*,10b*S*)-5a,10b-dihydro-1,3,5a,9-tetrahydroxy-8-methoxy-6*H*-benz[*b*]indeno[1,2-*d*]furan-6-one 5a-*O*-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside] (**1**), its *rel*-5a*S*,10b*R* isomer (**2**), and (2*R*,3*S*,4*S*)-3-*O*-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl]-3′-*O*-methyl-*ent*-epicatechin-(2α → *O* → 3,4α → 4)-(5a*S*, 10b*S*)-5a,10b-dihydro-1,3,5a,9-tetrahydroxy-8-methoxy-6*H*-benz[*b*]indeno[1,2-*d*]furan-6-one 5a-*O*-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside] (**3**). The structures were elucidated on the basis of analyses of chemical and spectroscopic evidence.

1. Introduction

Kaempferia parviflora Wall., which has a black rhizome, belongs to the family Zingiberaceae. In the northeast of Thailand, the rhizomes of *K. parviflora* have been used for the treatment of colic disorder as well as peptic and duodenal ulcers (Yenjai et al., 2004). Recently, various bioactivities of extracts of *K. parviflora* and/or methoxyflavones isolated from this plant, have been reported. These include: gastroprotective effects in rats (Rujjanawate et al., 2005); effects on P-glycoprotein function (Patanasethanont et al., 2006); inhibition of viral proteases (Sookkongwaree et al., 2006) and promotion of nitric oxide production (Wattanapitayakul et al., 2007). Some methylated flavonoids have also previously been isolated from *K. parviflora* (Jaipetch et al., 1983; Yenjai et al., 2004). However, the polar components of this plant have not been identified. In the course of our study on phytochemical constituents of the Zingiberaceae plant (Kikuzaki et al., 2001; Kikuzaki and Tesaki, 2002; Akiyama et al., 2006), the structure elucidation of three new compounds (**1**–**3**) isolated from the H_2O-soluble fraction of an extract of rhizomes of this plant is reported.

2. Results and discussion

Freeze–dried rhizomes of *K. parviflora* were successively extracted with CH_2Cl_2 and 70% aqueous acetone. After the evaporation of the acetone, the aqueous residue was extracted with EtOAc. The CH_2Cl_2 extract and EtOAc-soluble fraction were separated by column chromatography using silica gel, Sephadex LH-20 and Chromatorex ODS, respectively, to obtain 14 flavones, two flavanones, a chalcone, a diarylheptanoid, β-sitosteryl myristate, methyl linolate, three glyceroglycolipids and a sphingoglycolipid. The H_2O-soluble fraction was subjected to successive column chromatography using Sephadex LH-20 and ODS to give three new compounds (**1**–**3**) (see Fig. 1) and two known flavonol glycosides. The structures of the known compounds were identified by comparison of their spectroscopic data with those in the literature as 5-hydroxy-3,7-dimethoxyflavone (Jaipetch et al., 1983), 5-hydroxy-3,7,4′-trimethoxyflavone (Dong et al., 1999), 3,5,7-trimethoxyflavone (Joseph-Nathan et al., 1981), 3,5,7,4′-tetramethoxyflavone (Joseph-Nathan et al., 1981), 5,7-dimethoxyflavone (Jaipetch et al., 1983; Joseph-Nathan et al., 1981), 5,7,4′-trimethoxyflavone (Jaipetch et al., 1983; Joseph-Nathan et al., 1981), 5-hydroxy-7,4′-dimethoxyflavone (Gonzalez et al., 1989), 5-hydroxy-7-methoxyflavone (Asakawa, 1971), 5-hydroxy-3,7,3′,4′-tetramethoxyflavone (Vidari et al., 1971), 5,3′-dihydroxy-3,7,4′-trimethoxyflavone (Dong et al., 1999; Wang et al., 1989), 3,5,7,3′,4′-pentamethoxyflavone (Dong et al., 1999; Joseph-Nathan et al., 1981), 5-hydroxy-7,3′,4′-trimethoxyflavone (Ahond et al., 1990), 4′-hydroxy-5,7-dimethoxyflavone (Kao et al., 2004), 5,7,3′,4′-tetramethoxyflavone (Joseph-Nathan et al., 1981), (2*S*)-5-hydroxy-7-methoxyflavanone (Gonzalez et al., 1989; Su et al., 2003), (2*S*)-5,7-dimethoxyflavanone (Bick et al., 1972), (*E*)-2′-hydroxy-4′,6′-dimethoxychalcone (Jhoo et al., 2006), (1*E*,6*E*)-1,7-diphenyl-1,6-heptadiene-3,5-dione (Matthes et al., 1980), β-sitosteryl myristate (Parmar et al., 1998), methyl 9*Z*,12*Z*-octadecadienoate, 1-*O*-(9*Z*,12*Z*-octadecadienoyl)-3-*O*-[α-galactopyranosyl-(1 → 6)-β-galactopyranosyl]glycerol (Yoshikawa et al., 1992, 1994), 1-*O*-hexadecanoyl-3-*O*-[α-galactopyranosyl-(1 → 6)-β-galactopyranosyl]glycerol (Murakami et al., 1994), 1-*O*-hexadecanoyl-2-*O*-(9*Z*,12*Z*-octadecadienoyl)-3-*O*-[α-galactopyranosyl-(1 → 6)-β-galactopyranosyl]glycerol (Jung et al., 1996; Murakami et al., 1991), 1-*O*-β-glucopyranosyl-(8*Z*)-2-(2-hydroxytetra-

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cosanoylamino)-8-octadecene-1,3,4-triol (Kang et al., 2001; Tuntiwachwuttikul et al., 2004), quercetin 3-*O*-[α-rhamnopyranosyl-(1 → 6)-β-glucopyranoside] and isorhamnetin 3-*O*-[α-rhamnopyranosyl-(1 → 6)-β-glucopyranoside] (Beck and Haberlein, 1999).

Compound **1** was isolated as a brownish amorphous solid with a negative optical rotation $\left([\alpha]_D^{25} - 131.3\right)$. In the FABMS, a molecular ion peak was observed at *m*/*z* 625 $[M + H]^+$. The molecular formula was established as $C_{28}H_{32}O_{16}$ by HRFABMS measurement. In the ^{1}H NMR spectrum, doublets for *meta*-coupled protons [δ5.85 (1H, *d*, *J* = 2.0 Hz, H-8) and 5.98 (1H, *d*, *J* = 2.0 Hz, H-6)] indicated the presence of a 1,2,3,5-tetrasubstituted phenyl moiety. Signals for two additional aromatic protons [δ7.22 (1H, *s*, H-2′) and 7.34 (1H, *d*, *J* = 1.0 Hz, H-5′)] and a methine proton at δ5.17 (1H, *br s*, H-4) were observed. Furthermore, methoxy protons [δ3.89 (3H, *s*)], which showed a NOESY correlation with H-2′, were observed. The ^{13}C NMR spectrum showed the signals of one carbonyl carbon [δ196.1 (C-2)] and one acetal carbon [δ112.6 (C-3)]. In the HMBC experiment with **1**, correlations were observed between the following protons and carbons (H-4 and C-2, 3, 5, 9, 10, 1′, 6′; H-2′ and C-2, 1′, 3′, 4′, 6′; H-5′ and C-4, 1′, 3′, 4′, Fig. 2), indicating that the aglycone of **1** was 5a,10b-dihydro-1,3,5a,9-tetrahydroxy-8-methoxy-6*H*-benz[*b*]indeno[1,2-*d*]furan-6-one. In the ^{1}H NMR spectrum for **1**, the signals of two anomeric protons at δ4.54 and 4.66 showed the presence of two sugar moieties. The sugars were determined to be β-glucopyranose and α-rhamnopyranose based on observed coupling constants as well as comparison to the carbon chemical shifts of isorhamnetin 3-*O*-[α-rhamnopyranosyl-(1 → 6)-β-glucopyranoside] (Beck and Haberlein, 1999). In addition, acid hydrolysis of **1** afforded D-glucose and L-rhamnose whose structures were confirmed by co-HPLC analysis of their 1-[(*S*)-*N*-acetyl-α-methylbenzylamino]-1-deoxyalditol acetate derivatives with the same derivatives of standard sugars. The anomeric proton of glucose (δ4.54) was correlated to C-3 of the aglycone and H-1 of rhamnose (δ4.66) to C-6 of glucose (δ67.0), which indicated that 6-α-L-rhamnopyranosyl β-D-glucopyranose was attached to C-3. Compound **1** was acetylated by Ac_2O in pyridine to give a nonaacetyl derivative of **1**, and three phenolic acetyl methyl signals [δ2.26 (3H, *s*), 2.35 (3H, *s*) and 2.43 (3H, *s*)] were observed in the ^{1}H NMR spectrum. This result confirmed the presence of three phenolic hydroxy group in **1**. In the NOESY experiment with **1**, the correlation between H-4 and the anomeric proton of glucose indicated a *cis* relationship between C-3 and H-4 (Fig. 3). Thus, compound **1** was determined to be *rel*-(5a*S*,10b*S*)-5a,10b-dihydro-1,3,5a,9-tetrahydroxy-8-methoxy-6*H*-benz[*b*]indeno[1,2-*d*]furan-6-one 5a-*O*-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside]. To our knowledge, this is the first report of a 6*H*-benz[*b*]indeno[1,2-*d*]furan-6-one-type compound as a natural product.

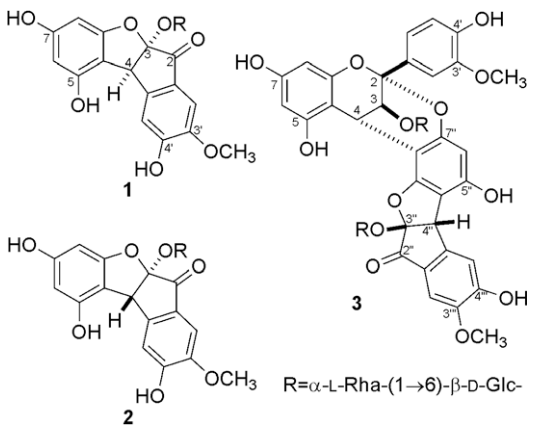

Fig. 1. Structures of compounds **1**–**3**.

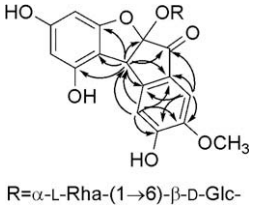

Fig. 2. Key HMBC correlations for compound **1**.

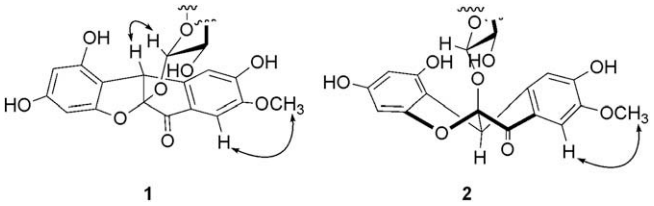

Fig. 3. Key NOESY correlations for compounds **1** and **2**.

Compound **2** was obtained as a brownish amorphous solid. The HRFABMS gave an $[M + H]^+$ peak at *m*/*z* 625.1762 corresponding to the same molecular formula ($C_{28}H_{32}O_{16}$) as **1**. The spectroscopic data of **2** were very similar to those of **1** except for the optical rotation $\left([\alpha]_D^{25} + 138.3\right)$ and the proton and carbon signals at the 4-position of aglycone and the 1- and 5-positions of the glucose moiety. Its structure was elucidated to be the same as **1** by HMQC, HMBC, and NOESY experiments. The absence of a correlation in the NOESY experiment between H-4 (δ4.82) and the anomeric proton (δ4.90) of glucose confirmed the *trans* stereochemistry of **2** (Fig. 3). As with **1**, acid hydrolysis of **2** yielded D-glucose and L-rhamnose. Therefore, the structure of **2** was identified as *rel*-(5a*S*,10b*R*)-5a,10b-dihydro-1,3,5a,9-tetrahydroxy-8-methoxy-6*H*-benz[*b*]indeno[1,2-*d*]furan-6-one 5a-*O*-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside].

Compound **3** was obtained as a brownish amorphous solid. An $[M + H]^+$ peak at *m*/*z* 1233 was observed in the FABMS experiment, and the molecular formula $C_{56}H_{64}O_{31}$ was established by HRFABMS measurement. The ^{13}C and ^{1}H NMR spectra of **3** showed many similarities to those of **1**. A key difference in the ^{1}H NMR spectrum was the presence of the singlet at δ6.17 instead of *meta*-coupled signals of the 6- and 8-positions (δ5.85 and 5.98) in **1**. Additionally, five aromatic protons [δ5.80 (1H, *d*, *J* = 2.2 Hz, H-8), 5.81 (1H, *d*, *J* = 2.2 Hz, H-6), 6.84 (1H, *d*, *J* = 8.5 Hz, H-5′), 7.17 (1H, *dd*, *J* = 8.5, 2.0 Hz, H-6′) and 7.26 (1H, *d*, *J* = 2.0 Hz, H-2′)] were observed in the ^{1}H NMR spectrum of **3**, suggesting the presence of a 1,2,4-trisubstituted phenyl and 1,2,3,5-tetrasubstituted phenyl moieties. Two methine protons at δ4.50 (1H, *d*, *J* = 3.7 Hz, H-3) and 4.90 (1H, *d*, *J* = 3.7 Hz, H-4) and an acetal carbon [δ100.0 (C-2)] were also observed. Long-range correlations in the HMBC spectrum were observed between the following protons and carbons: H-4 and C-2, 3, 5, 9, 10; H-2′ and C-2; H-6′ and C-2. In addition, methoxy protons (δ3.89, 3H, *s*) were correlated to H-2′ in the NOESY spectrum. These results and comparison with the NMR spectroscopic data of A-linked proanthocyanidin (Lou et al., 1999; Hatano et al., 2002) suggest that the 3′-*O*-methylepicatechin moiety was connected to **1** as in proanthocyanidin type-A. In the HMBC spectrum, both H-4 and a proton at δ6.17 were correlated with a carbon at δ155.1, and H-4 and H-4″ (δ5.33) with a carbon at δ158.5, suggesting that C-4 was attached to C-6″ or 8″ and C-2 linked C-5″ or 7″ through an ether linkage. Acetylation of **3** gave a heptadecaacetyl derivative (**3a**) having five phenolic acetyl groups [δ2.20 (3H, *s*), 2.31 (3H, *s*), 2.32 (3H, *s*), 2.42 (3H, *s*) and 2.59

(3H, *s*)]. In the HMBC spectrum of **3a**, a proton at δ6.56 and H-4″ (δ5.05) were correlated with a carbon at δ145.7 (C-5″). The upfield shift of this carbon signal, compared with that of **3** (δ154.0) indicated that the C-5″ position was acetylated (Ewing, 1979) and the signal at δ6.56 was assignable to H-6″. Thus, the 2- and 4-positions of the methylepicatechin moiety were connected to 7″-*O* and C-8″, respectively. The presence of two 6-α-L-rhamnopyranosyl-D-glucopyranose moieties was confirmed by the ^{1}H and ^{13}C NMR spectroscopic data of **3** and acid hydrolysis of **3**. In addition, complete assignments of protons of two disaccharide units were achieved by TOCSY experiment. In the HMBC spectrum, cross-peaks were observed from two anomeric protons of glucose moieties at δ4.53 and 4.70 to C-3 (δ70.1) and C-3″ (δ112.8) carbons, respectively. The relative stereochemistry of **3** was determined on the basis of the coupling constants in the ^{1}H NMR spectrum and the NOESY experiment. With regard to the methylcatechin part, the 2,3-*trans* form was identified by comparison of the coupling constant of H-3 (3.7 Hz) with that in the literature (Lou et al., 1999). The NOESY correlation between H-4″ and the glucose anomeric proton (δ4.70) indicated a *cis* relationship with the group attached to C-3″. Furthermore, a cross-peak between H-6 and H-2‴ was observed. The upfield shifts of H-2‴ (δ6.99) and the OCH_3 at C-3‴ (δ3.50), compared with those of **1**, were considered to be caused by shielding of the A-ring in the catechin moiety (Fig. 4). A negative Cotton effect at short wavelength ($[\theta]_{213}$–157,000) in the CD spectrum of **3** was consistent with the 4*S* absolute configuration (Hatano et al., 2002; Barrett et al., 1979; Kolodziej et al., 1991). These results indicated the absolute configuration of **3** to be 2*R*, 3*S*, 4*S*, 3″*S*, and 4″ *S*. Thus, compound **3** was determined to be (2*R*,3*S*,4*S*)-3-*O*-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl]-3′-*O*-methyl-*ent*-epicatechin-(2α → *O* → 3,4α → 4)-(5a*S*,10b*S*)-5a,10b-dihydro-1,3,5a,9-tetrahydroxy-8-methoxy-6*H*-benz[*b*]indeno-[1,2-*d*]furan-6-one 5a-*O*-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside].

Recently, Es-Safi et al. reported that compounds having the same skeleton as **1** and **2** were formed as artifacts from malvidin 3-*O*-glucoside incubated in an ethanolic solution at 40 °C for several days. They proposed that such compounds might be formed through addition of water on C-2 position of malvidin followed by oxidation (Es-Safi et al., 2008). Therefore, we conducted the following experiment to ascertain whether or not compounds **1**–**3** were artifacts derived in the extraction and purification process. Immediately on extraction of freeze–dried rhizomes of *K. parviflora* with 3% TFA in 70% aqueous MeOH, HPLC analysis of the extract was performed using an acidic eluate to detect **1**–**3** (t_R 6.8, 5.7 and 12.1 min, respectively) together with some compounds having absorption maximum at 520 nm which were expected to be anthocyanins (t_R of 7.7, 8.9, 15.8 and 18.8 min). This finding indicated that compounds **1**–**3** were not artifacts of the extraction and purification process of the rhizomes of *K. parviflora*. Further study on structure determination of anthocyanins are now in progress.

3. Conclusions

Three new phenolic glycosides (**1**–**3**) having a rare skeleton, were isolated from the rhizomes of *K. parviflora*. A feature of these compounds was the 6*H*-benz[*b*]indeno[1,2-*d*]furan-6-one substructure. A further characteristic of **3** was that 3′-*O*-methylepicatechin unit was connected to the benz[*b*]indeno[1,2-*d*]furan skeleton through both C–C bond and ether linkage as A type proanthocyanidins.

4. Experimental

4.1. General experimental procedures

Optical rotations were recorded on a JASCO P1030 polarimeter (Tokyo, Japan). The CD spectrum was recorded on a JASCO J-820 spectropolarimeter. UV spectra were measured on a Shimadzu UV-2500PC UV–Vis spectrophotometer. ^{1}H, ^{13}C, and 2D NMR spectra were obtained on a Varian Unity 500 spectrometer (500 MHz, Varian Inc., Palo Alto, CA) using TMS as an internal standard. FAB and HRFABMS were measured using glycerol as the matrix on a JEOL JMS-700T mass spectrometer. HPLC analysis was carried out with a JASCO PU-980 Intelligent Pump equipped with a JASCO MD-910 Multiwavelength Detector. The column for HPLC was a Mightysil Si 60 (5 μm, 250 × 4.6 mm, Kanto Chemical). Si gel 60

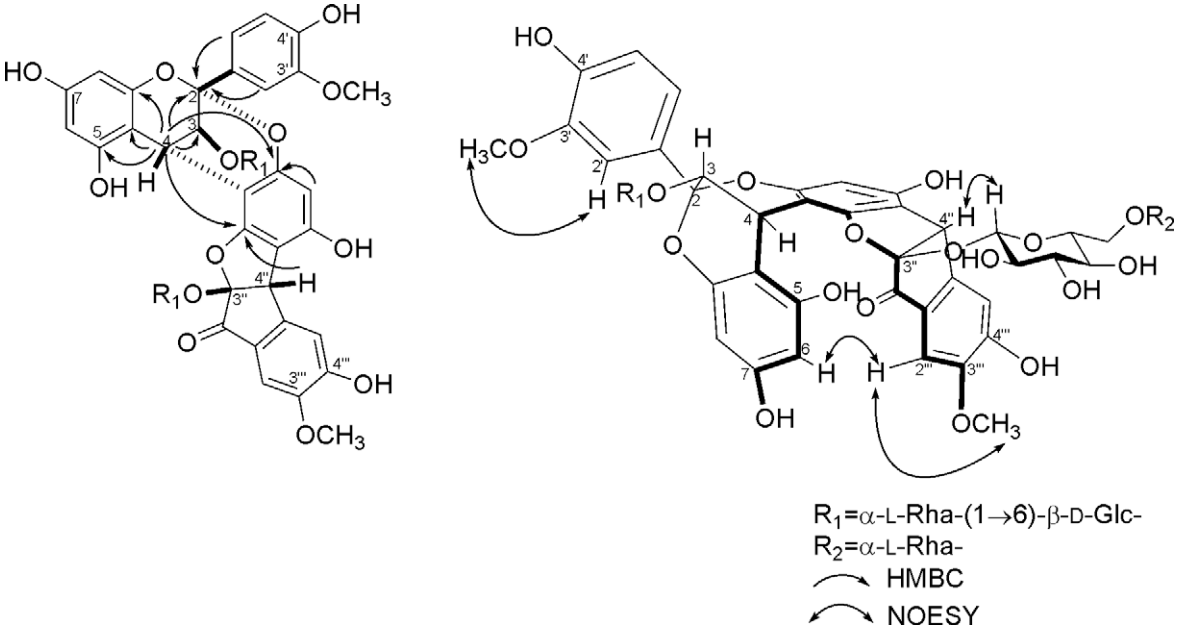

Fig. 4. Key HMBC and NOESY correlations for compound **3**.

(70–230 mesh, Merck), Sephadex LH-20 (Pharmacia) and Chromatorex ODS DM1020T (100-200 mesh, Fuji Silysia Chemical) were used for column chromatography.

4.2. Plant material

Rhizomes of *K. parviflora* from Thailand were supplied by Taiyo Co., Osaka, Japan. (Lot. No. CP000135820LA).

4.3. Extraction and isolation

Freeze–dried rhizomes (1960 g) of *K. parviflora* were extracted with CH_2Cl_2 at room temperature to afford a crack of extract (131.8 g). The residue was further extracted with aqueous acetone (3:7, v/v). After filtration, the acetone was evaporated under reduced pressure and an aqueous extract was obtained. The latter was partitioned between EtOAc and H_2O to give the EtOAc-soluble (31.8 g) and H_2O-soluble fractions (112.6 g). The CH_2Cl_2 extract (62.5 g) was subjected to silica gel CC using benzene-acetone to give 42 fractions. Fractions 6, 11, 14, 18, 22, 25, 28, 32 and 36 were recrystallized to obtain 5-hydroxy-3,7-dimethoxyflavone (384 mg), 5-hydroxy-3,7,4′-trimethoxyflavone (106 mg), 5-hydroxy-7,4′-dimethoxyflavone (858 mg), 5-hydroxy-3,7,3′,4′-tetramethoxyflavone (15 mg), 5,3′-dihydroxy-3,7,4′-trimethoxyflavone (29 mg), 3,5,7-trimethoxyflavone (146 mg), 3,5,7,4′-tetramethoxyflavone (21 mg), 5,7-dimethoxyflavone (7 mg) and 5,7,4′-trimethoxyflavone (2023 mg), respectively. Fractions 1 and 2 were purified by using silica gel CC (*n*-hexane-acetone, 99:1) to yield *β*-sitosteryl myristate (6 mg). Fractions 3 and 4 were separated by silica gel CC (*n*-hexane-acetone, 97:3) to yield (2*S*)-5-hydroxy-7-methoxyflavanone (8 mg), (*E*)-2′-hydroxy-4′,6′-dimethoxychalcone (3 mg) and (1*E*,6*E*)-1,7,diphenyl-1,6-heptadiene-3,5-dione (5 mg). Fraction 7 was re-applied to a silica gel column (benzene) to give 5-hydroxy-7-methoxyflavone (11 mg). Fractions 19 and 20 were separated by silica gel (benzene-MeOH, 99:1) and ODS (MeOH–H_2O, 4:1) CC to yield 5-hydroxy-7,3′,4′-trimethoxyflavone (106 mg) and (2*S*)-5,7-dimethoxyflavanone (3 mg). 3,5,7,3′,4′-Pentamethoxyflavone (132 mg) was obtained from fraction 32 by CC using silica gel (CH_2Cl_2-acetone, 19:1). The EtOAc-soluble fraction (27.9 g) was fractionated by silica gel CC using benzene-acetone to give 29 fractions. Fraction 22 was purified by silica gel CC (CH_2Cl_2-acetone, 19:1) to afford 4′-hydroxy-5,7-dimethoxyflavone (8 mg) and 5,7,3′,4′-tetramethoxyflavone (11 mg). Fraction 24 was purified by silica gel CC (CH_2Cl_2-acetone, 19:1) to give 1-*O*-*β*-glucopyranosyl-(8*Z*)-2-(2-hydroxytetracosanoylamino)-8-octadecene-1,3,4-triol (14 mg). Fraction 26 was subjected to be Sephadex LH-20 (MeOH) and silica gel (EtOAc–MeOH–H_2O, 17:2:1) CC to yield 1-*O*-hexadecanoyl-3-*O*-[α-galactopyranosyl-(1 → 6)-*β*-galactopyranosyl]-glycerol (9 mg) and 1-*O*-hexadecanoyl-2-*O*-(9*Z*,12*Z*-octadecadienoyl)-3-*O*-[α-galactopyranosyl-(1 → 6)-*β*-galactopyranosyl]-glycerol (67 mg). Fraction 27 was separated by CC using Sephadex LH-20 (MeOH) and ODS gel (MeOH–H_2O, 9:1) to obtain methyl 9*Z*,12*Z*-octadecadienoate (12 mg) and 1-*O*-(9*Z*,12*Z*-octadecadienoyl)-3-*O*-[α-galactopyranosyl-(1 → 6)-*β*-galactopyranosyl]-glycerol (4 mg). The H_2O-soluble fraction (35.5 g) was subjected to Sephadex LH-20 CC using H_2O, H_2O–MeOH (1:1, v/v), and MeOH to yield 20 fractions. Fractions 11–15, eluted by MeOH–H_2O (1:1, v/v) were rechromatographed separately. Fraction 11 (650 mg) was subjected to ODS CC (MeOH–H_2O, 3:7) to yield compounds **1** (68 mg) and **2** (72 mg). Fraction 12 (340 mg) was purified by ODS gel (MeOH–H_2O, 3:7) to give isorhamnetin 3-*O*-[α-rhamnopyranosyl-(1 → 6)-*β*-glucopyranoside] (5 mg). Compound **3** (55 mg) was obtained from fraction 13 (290 mg) by CC using ODS gel (MeOH–H_2O, 3:7). Fraction 15 (105 mg) was rechromatographed on ODS gel (MeOH–H_2O, 45:55) to yield quercetin 3-*O*-[α-rhamnopyranosyl-(1 → 6)-*β*-glucopyranoside] (6 mg).

Table 1
NMR spectroscopic data (500 MHz, CD_3OD) for compounds **1** and **2**[a]

Position	**1**		**2**	
	δ_H (*m*, *J* in Hz)	δ_C	δ_H (*m*, *J* in Hz)	δ_C
2		196.1		196.0
3		112.6		113.3
4	5.17 (*br s*)	49.7	4.82 (*br s*)	51.3
5		161.7		161.6
6	5.98 (*d*, 2.0)	97.7	5.94 (*d*, 2.0)	97.4
7		160.8		160.8
8	5.85 (*d*, 2.0)	90.1	5.86 (*d*, 2.0)	90.8
9		156.0		155.9
10		105.5		105.4
1′		124.7		125.9
2′	7.22 (*s*)	106.2	7.22 (*s*)	106.3
3′		150.8		150.7
4′		158.5		157.6
5′	7.34 (*d*, 1.0)	113.7	7.33 (*d*, 0.7)	113.7
6′		152.4		150.5
Glc-1	4.54 (*d*, 7.6)	99.2	4.90 (*m*)	100.3
Glc-2	3.29 (*m*)	74.7	3.20 (*dd*, 9.3, 7.8)	74.8
Glc-3	3.30 (*m*)	77.5	3.35 (*m*)	77.9
Glc-4	3.37 (*dd*, 9.8, 9.0)	70.8	3.27 (*m*)	71.3
Glc-5	3.03 (*ddd*, 9.8, 4.6, 2.0)	77.0	3.27 (*m*)	77.3
Glc-6a	3.90 (*dd*, 10.7, 2.0)	67.0	3.86 (*br d*, 10.7)	67.4
Glc-6b	3.51 (*dd*, 10.7, 4.6)		3.51 (*br d*, 10.7)	
Rha-1	4.66 (*d*, 1.7)	101.8	4.70 (*d*, 1.7)	102.0
Rha-2	3.92 (*dd*, 3.4, 1.7)	72.1	3.90 (*dd*, 3.4, 1.7)	72.2
Rha-3	3.69 (*dd*, 9.8, 3.4)	72.3	3.72 (*dd*, 9.5, 3.4)	72.3
Rha-4	3.35 (*dd*, 9.8, 9.5)	74.1	3.35 (*dd*, 9.8, 9.5)	74.2
Rha-5	3.64 (*dq*, 9.5, 6.3)	69.7	3.61 (*dq*, 9.8, 6.1)	69.7
Rha-6	1.26 (*d*, 6.3)	18.0	1.21 (*d*, 6.1)	18.0
OCH_3	3.89 (*s*)	56.5	3.89 (*s*)	56.6

[a] Chemical shifts are shown in *δ* values (ppm) relative to the solvent peak.

4.4. Compound **1**

Brownish amorphous solid; $[\alpha]_{max}^{MeOH}$ − 131.3° (*c* 1.0, MeOH); UV λ_{max}^{MeOH} nm (log *ε*) 236 (4.3), 283 (4.0), 326 (4.0); for ^1H and ^{13}C NMR spectroscopic data, see Table 1; FABMS *m*/*z* 625 $[M + H]^+$, 317; HRFABMS *m*/*z* 625.1769 $[M + H]^+$ (calcd for $C_{28}H_{33}O_{16}$, 625.1768).

4.5. Acetylation of compound **1**

To a solution of compound **1** (3.0 mg) in pyridine (0.5 ml) was added an excess of Ac_2O (0.5 ml) and the mixture was allowed to stand overnight at room temperature. The reaction mixture was partitioned between H_2O and EtOAc. The EtOAc layer was washed with satd. NaCl aq. and evaporated to give compound **1a** (4.1 mg). Compound **1a**: pale yellow amorphous solid; ^1H NMR (500 MHz, $CDCl_3$) *δ*1.16 (3H, *d*, *J* = 6.1 Hz, Rha-6), 1.97, 2.01, 2.037, 2.040, 2.09, 2.11, 2.26, 2.35, 2.43 (each 3H, *s*, $COCH_3$), 3.55 (1H, *m*, Glc-6b), 3.66 (2H, *m*, Glc-5, 6a), 3.87 (1H, *m*, Rha-5), 3.87 (3H, *s*, OCH_3), 4.74 (1H, *br s*, Rha-1), 4.93 (1H, *br s*, H-4), 5.00–5.26 (7H, *m*, Glc-1,2,3,4, Rha-2,3,4), 6.63 (1H, *dd*, *J* = 2.0, 0.5 Hz, H-8), 6.66 (1H, *d*, *J* = 2.0 Hz, H-6), 7.33 (1H, *s*, H-2′), 7.34 (1H, *d*, *J* = 0.7 Hz, H-5′); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*17.4 (Rha-6), 20.7–21.3 ($COCH_3$), 49.9 (C-4), 56.4 (OCH_3), 66.5 (Rha-5), 66.9 (Glc-6), 69.0–72.6 (Glc-2,3,4, Rha-2,3,4), 73.0 (Glc-5), 95.7 (Glc-1), 97.9 (Rha-1), 102.6 (C-8), 107.0 (C-2′), 109.9 (C-6), 110.8 (C-3), 116.3 (C-10), 120.7 (C-5′), 131.4 (C-1′), 143.4 (C-6′), 146.6 (C-5), 147.7 (C-4′), 152.1 (C-7), 152.6 (C-3′), 159.3 (C-9), 167.9 ($COCH_3$), 168.0 ($COCH_3$), 168.7 ($COCH_3$), 169.5 ($COCH_3$), 169.6 ($COCH_3$), 169.8 ($COCH_3$), 169.9 ($COCH_3$), 170.2 ($COCH_3$), 170.3 ($COCH_3$), 191.6 (C-2).

Table 2
NMR spectroscopic data (500 MHz) for compounds **3** and **3a**

Position	**3**[a]		**3a**[b]	
	δ_H (*m*, *J* in Hz)	δ_C	δ_H (*m*, *J* in Hz)	δ_C
Aglycone				
2		100.0		98.0
3	4.50 (*d*, 3.7)	70.1	4.44 (*d*, 3.2)	70.0
4	4.90 (*d*, 3.7)	24.9	4.56 (*m*)	26.2
5		156.4		147.6
6	5.81 (*d*, 2.2)	97.3	6.53 (*d*, 2.2)	109.7
7		158.5		150.1
8	5.80 (*d*, 2.2)	95.3	6.57 (*d*, 2.2)	107.1
9		154.1		152.8
10		105.3		114.1
1′		131.8		136.2
2′	7.26 (*d*, 2.0)	112.4	7.32 (*d*, 2.0)	112.1
3′		148.1		150.6
4′		147.9		140.5
5′	6.84 (*d*, 8.5)	115.5	7.09 (*d*, 8.3)	122.3
6′	7.17 (*dd*, 8.5, 2.0)	121.3	7.23 (*dd*, 8.3, 2.0)	119.6
2″		196.0		191.4
3″		112.8		111.4
4″	5.33 (*d*, 0.7)	49.4	5.05 (*d*, 0.7)	49.6
5″		154.0		145.7
6″	6.17 (*s*)	97.5	6.56 (*s*)	104.5
7″		155.1		153.0
8″		100.1		103.0
9″		158.5		157.0
10″		107.2		112.3
1‴		124.6		131.3
2‴	6.99 (*br s*)	106.4	7.32 (*br s*)	107.2
3‴		150.5		152.5
4‴		158.5		147.7
5‴	7.32 (*br s*)	113.6	7.32 (*br s*)	120.5
6‴		152.3		144.2
3′-OCH_3	3.89 (*s*)	56.7	3.92 (*s*)	56.2
3‴-OCH_3	3.50 (*br s*)	56.1	3.83 (*s*)	56.3
C-3 sugar				
Glc-1	4.53 (*d*, 7.6)	99.6	4.56 (*m*)	95.0
Glc-2	2.95 (*dd*, 9.3, 7.6)	75.2	4.65 (*m*)	68.6–73.0
Glc-3	3.55 (*m*)	77.2	5.14 (*m*)	68.6–73.0
Glc-4	3.12 (*dd*, 9.3, 9.0)	71.7	4.79 (*m*)	68.6–73.0
Glc-5	3.45 (*m*)	76.9	3.56 (*m*)	72.4
Glc-6a	3.91 (*m*)	68.1	3.52 (*m*)	67.1
Glc-6b	3.45 (*m*)		3.32 (*m*)	
Rha-1	4.65 (*d*, 1.7)	102.2	4.62 (*m*)[c]	98.01[f]
Rha-2	3.72 (*dd*, 3.4, 1.7)	72.1	5.02–5.21 (*m*)	68.6–73.0
Rha-3	3.58 (*m*)	72.3	5.02–5.21 (*m*)	68.6–73.0
Rha-4	3.28 (*m*)	73.9	5.02–5.21 (*m*)	68.6–73.0
Rha-5	3.55 (*m*)	69.8	3.76 (*m*)[d]	66.5[g]
Rha-6	1.17 (*d*, 6.1)	17.9	1.17 (*d*, 6.1)[e]	17.3[h]
C-3″ sugar				
Glc-1	4.70 (*d*, 7.6)	99.4	5.34 (*d*, 8.1)	97.3
Glc-2	3.33 (*m*)	75.4	5.02 (*m*)	68.6–73.0
Glc-3	3.66 (*m*)	76.4	5.37 (*dd*, 9.5, 9.3)	68.6–73.0
Glc-4	3.35 (*m*)	71.1	5.19 (*m*)	68.6–73.0
Glc-5	3.29 (*m*)	76.5	3.66 (*m*)	72.9
Glc-6a	3.92 (*m*)	67.1	3.69 (*m*)	67.7
Glc-6b	3.51 (*m*)		3.63 (*m*)	
Rha-1	4.66 (*d*, 1.7)	101.8	4.76 (*d*, 1.5)[c]	98.05[f]
Rha-2	3.94 (*dd*, 3.4, 1.7)	72.1	5.02–5.21 (*m*)	68.6–73.0
Rha-3	3.71 (*dd*, 9.8, 3.4)	72.3	5.02–5.21 (*m*)	68.6–73.0
Rha-4	3.35 (*m*)	74.1	5.02–5.21 (*m*)	68.6–73.0
Rha-5	3.64 (*m*)	69.7	3.91 (*m*)[d]	66.6[g]
Rha-6	1.23 (*d*, 6.3)	18.0	1.18 (*d*, 6.1)[e]	17.5[h]

[a] Recorded in CD_3OD. Chemical shifts are shown in δ values (ppm) relative to the solvent peak.
[b] Recorded in $CDCl_3$. Phenolic acetyl methyl protons were detected at δ2.20, 2.31, 2.32, 2.42 and 2.59 (each, 3H, *s*), glycosyl acetyl methyl protons were detected at δ1.949 (3H, *s*), 1.954 (6H, *s*), 1.96, 1.99, 2.02, 2.04, 2.050, 2.053, 2.07, 2.12 and 2.17 (each, 3H, *s*), acetyl methyl carbons were detected in the range of δ20.5–21.3 and acetyl carbonyl carbons were detected in the range of δ168.0–170.2.
[c–h] Assignments with the same superscript may be interchanged.

4.6. Compound **2**

Brownish amorphous solid: $[\alpha]_D^{25}$ + 138.3° (*c* 1.0, MeOH); UV λ_{max}^{MeOH} nm (log ε) 236 (4.3), 280 (4.0), 322 (3.9); for ^1H and ^{13}C NMR spectroscopic data see Table 1; FABMS *m*/*z* 625 $[M+H]^+$, 317; HRFABMS *m*/*z* 625.1762 $[M+H]^+$ (calcd for $C_{28}H_{33}O_{16}$, 625.1768).

4.7. Compound **3**

Brownish amorphous solid; $[\alpha]_D^{25}$ − 131.3° (*c* 1.0, MeOH); CD (MeOH) $[\theta]_{205}$ +45,900, $[\theta]_{213}$ − 157,000, $[\theta]_{246}$ + 89,500, $[\theta]_{282}$ − 13,000, $[\theta]_{292}$ − 5720, $[\theta]_{322}$ − 23,700; UV λ_{max}^{MeOH} nm (log ε) 234 (4.6), 281 (4.1), 324 (3.9); for ^1H and ^{13}C NMR spectroscopic data see Table 2; FABMS *m*/*z* 1233 $[M+H]^+$, 617; HRFABMS (+NaI) *m*/*z* 1255.3334 $[M+Na]^+$ (calcd for $C_{56}H_{64}O_{31}Na$, 1255.3328).

4.8. Acetylation of compound **3**

Compound **3** (3.0 mg) was acetylated in the same way as compound **1** to give compound **3a** (4.1 mg). Compound **3a**: pale yellow solid; for ^1H and ^{13}C NMR spectroscopic data see Table 2.

4.9. Acid hydrolysis of compounds **1**, *2* and **3**

Solutions of compounds **1**, **2** and **3** (1.0 mg, each) in 2 M TFA (1 ml) were heated at 90 °C for 3 h. After cooling, MeOH was repeatedly added to and evaporated from the reaction mixture until the acid was completely removed. The residue was dissolved in H_2O (1 ml), to which a solution of (*S*)-α-methylbenzylamine (5 mg) and $NaBH_3CN$ (8 mg) in EtOH (1 ml) were added. After being allowed to stand overnight at room temperature, glacial AcOH (0.2 ml) was added to the reaction mixture. After evaporation, the residue was acetylated with Ac_2O (0.3 ml) in pyridine (0.3 ml) and the mixture was allowed to stand overnight at room temperature. After evaporation, H_2O (1 ml) was added and the solution was passed through a Sep-Pak C_{18} cartridge and washed with H_2O, CH_3CN–H_2O (1:4, v/v) and CH_3CN–H_2O (1:1, v/v) (each 5 ml), successively. The CH_3CN–H_2O (1:1, v/v) eluate was analyzed and the 1-[(*S*)-*N*-acetyl-α-methylbenzylamino]-1-deoxyalditol acetate derivatives were identified by co-HPLC analysis (column, Mightysil Si 60, 250 × 4.6 mm; solvent, *n*-hexane-EtOH, 9:1 v/v; flow rate, 1.0 ml/min; detection, UV absorbance at 200–300 nm) with derivatives of the standard sugars prepared under the same conditions (Oshima and Kumanotani, 1981; Shao et al., 2007). The derivatives of D-glucose and L-rhamnose were detected with t_R of 19.9 min and 13.8 min, respectively.

4.10. Extraction and HPLC analysis of compounds **1**, *2* and **3**

Freeze–dried rhizomes (100 mg) of *K. parviflora* were extracted with 3% TFA (1 ml) in MeOH–H_2O (3:7, v/v) (20 min × 2) at room temperature. After filtration, MeOH was evaporated under reduced pressure. An aqueous residue was washed with EtOAc and immediately analysed by HPLC (column, Mightysil RP-18 GP (5 μm, 250 × 4.6 mm, Kanto Chemical); solvent, 0.3% TFA in CH_3CN-0.3% TFA in H_2O, 3:17; flow rate, 1.0 ml/min; detection, UV absorbance at 200–600 nm). Compounds **1**–**3** were detected with t_R of 6.8, 5.7 and 12.1 min, respectively.

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