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Extractives of *Cercidiphyllum japonicum* twigs: isolation and structural elucidation of a new galloylflavonol glycoside, anomeric tannins and flavonoids

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Abstract: *Cercidiphyllum japonicum* is a deciduous tree that grows in East Asia, where its raw extracts have long been used in folk medicnes to treat various disorders or diseases. In the current work, extracts from *C. japonicum* twigs were studied for the first time. Seven individual compounds were isolated from the extracts, including a new galloylflavonol glycoside, namely 8-methoxykaempferol-4′-*O*-galloyl-3-*O*-α-L-rhamnopyranoside (**VII**), and six known phenolics [two anomeric galloyltannins (3,4,6-tri-*O*-galloyl-β-D-glucopyranoside (**I**) and 2,2′,5-tri-*O*-galloyl-α/β-D-hamamelose (**III**)), one anomeric ellagictannin, pedunculagin (**II**), one flavonol, kaempferol (**V**) and two flavonol derivatives (kaempferol-3-*O*-α-L-rhamnopyranoside (**IV**) and 8-methoxykaempferol (**VI**))]. Structural elucidation of **I**–**VII** was conducted mainly on the basis of their spectroscopic [ultraviolet (UV), infrared (IR), nuclear magnetic resonance (NMR), mass spectrometry (MS)] and physicochemical analysis, as well as by comparison of the analytical data with those in the literature. Compounds **I**, **II**, **IV** and **VI** have not yet been reported in the genus *Cercidiphyllum*. Compound **VII**, a previously undescribed flavonoid, was isolated and elucidated in this work for the first time.

Keywords: *Cercidiphyllum japonicum*, extractives, galloylflavonol glycoside, structure elucidation, twigs

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Introduction

Tremendous amounts of tree twigs are incinerated or considered as useless by-products and disposed of in landfills in the course of logging or pulping. Of course, landfills are problematic from an environmental point of view (Feng et al. 2013; Si et al. 2013). On the other hand, the extraneous components of twigs could be a source of value-added products as they may contain undetected compounds. It is also well known that extractives are also markers for chemotaxonomical differentiation of tree species (Si et al. 2009; Wang et al. 2016; Vidakovic et al. 2018). The biosynthesis routes of extractives are highly relevant from the scientific point of view (Tsao et al. 2016; Mangindaan et al. 2017). New extractives with various activities may also serve for the development of medicines (Si et al. 2016a, 2017; Belt et al. 2017).

Cercidiphyllum japonicum Sieb. et Zucc., also known as katsura, is a deciduous and broad-leaved tree, while *Cercidiphyllum* is the sole genus of the Cercidiphyllaceae family (Sarker et al. 1997; Kubo et al. 2010). This species is well represented in fossil records, with occurrence in the late Cretaceous and Tertiary of Europe and North America. "*Cercidiphyllum japonicum*" is distributed only in East Asian countries, such as China, Japan and Korea (Tada and Sakurai 1991; Sarker et al. 1997). The katsura trees grow in cool-temperate riparian forests, where they can reach up to 30 m in height and a trunk with ca. 2 m in diameter. The trees can survive 1000 years several hundred years up to 1000 years by shooting sprouts from the base. *Cercidiphyllum japonicum* is dioecious, blooms in early spring before the leaves shoot and is wind-pollinated (Teifel and Berger 1993; Isagi et al. 2005).

Plant extractives of *C. japonicum* have been widely used in traditional Asian medicines owing to their antiinflammatory, antimicrobial, antifungal and antioxidative activities. They are also used as hair growth promoting agents and for other activities (Takasugi and Katui 1986; Kasuga et al. 2008; Bae et al. 2017). The components of xylem extractives, such as kaempferol-7-*O*-β-glucopyroanside, quercetin-3-*O*-β-glucopyranoside, kaempferol-3-*O*-β-glucopyranoside and 8-methoxykaempferol-3-*O*-β-glucopyranoside exhibit

an anti-ice nucleation effect to promote supercooling of water (Wang et al. 2012). Our previous investigations on *C. japonicum* leaves and barks resulted in the extraction and separation of several phenolic compounds, including flavonoids, tannins and phenolic acids (Lee and Bae 2015; Lee et al. 2015, 2016; Bae et al. 2017). However, to the best of our knowledge, screening of the twig extractives of *C. japonicum* has never been carried out.

Aimed at the search for wood extractives, which may be responsible for the medicinal or pharmaceutical effects of the tree, the focus of the present paper was the isolation, purification and structural elucidation of three anomeric tannins and four flavonoid type components from the twigs of *C. japonicum*.

Materials and methods

Plant material: Fresh twigs from a 20-year-old *C. japonicum* tree were collected in the Xuchang area of Henan Province, P.R. China, in November 2016 and then were air-dried in the dark. Samples were authenticated by Prof. Dan Wang (Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing, P.R. China). A voucher specimen (No. TCJ-20161101) has been deposited in the herbarium of Plant Chemistry and Fine Chemicals Center, Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin, P.R. China.

Instruments: Ultraviolet (UV) spectroscopy was performed on a Jenway 6405 UV spectrophotometer (Jenway Ltd., Dunmow, UK). Infrared (IR) spectra were recorded on a Perkin-Elmer BX Fourier-transform infrared (FT IR) spectrometer (Perkin-Elmer Inc., Wellesley, MA, USA)

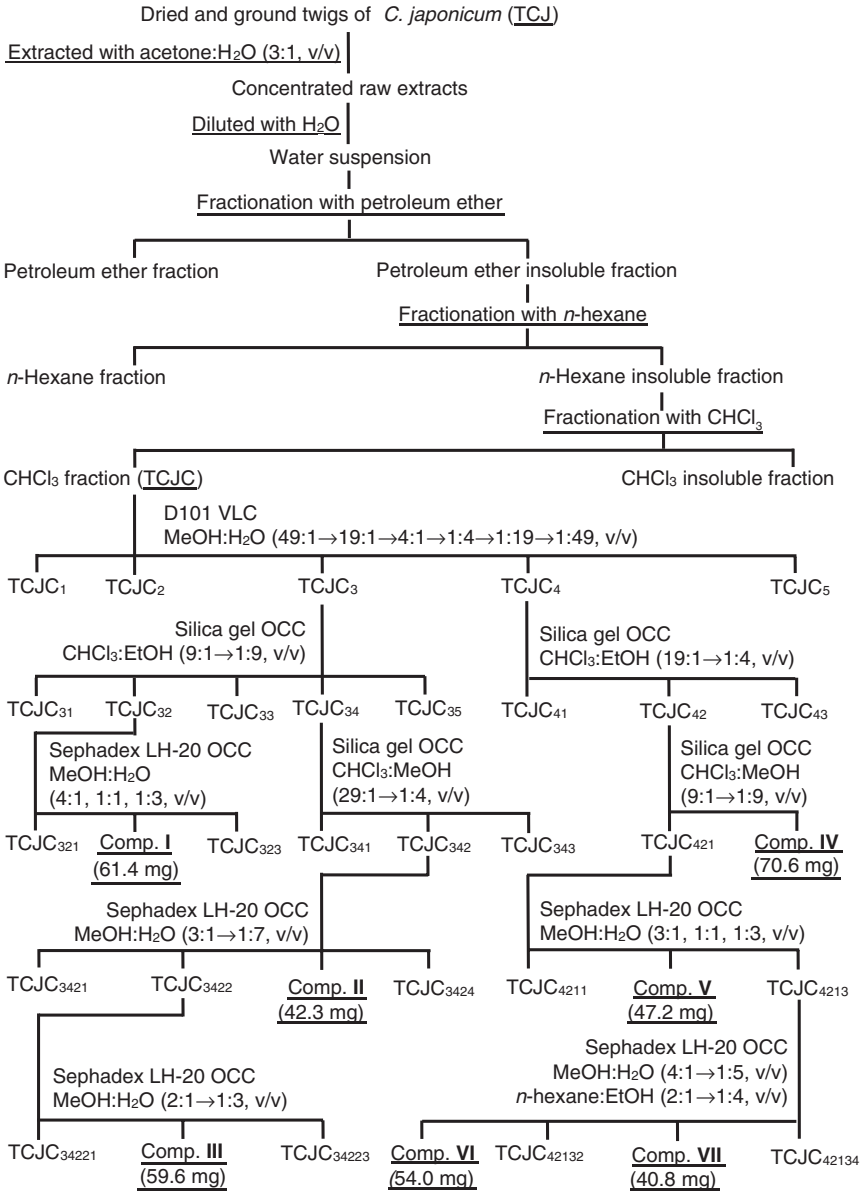


Figure 1: Flowchart of extraction, fractionation and purification of extractives from the twigs of *C. japonicum*.

using the KBr disk method. Optical rotations were determined using a Perkin Elmer 341 polarimeter (Perkin-Elmer, Waltham, MA, USA). An Electro-thermal 9100 apparatus (Shimadzu, Japan) was used to measure the melting point (mp, uncorrected). All nuclear magnetic resonance (NMR) spectra were obtained on a Bruker Avance DPX 400 instrument (Rheinstetten, Germany) performed at 400 and 100 MHz for hydrogen and carbon, respectively, in dimethyl sulfoxide-d6 (DMSO-d_6) with tetramethylsilane as an internal standard. Chemical shifts are given in ppm and the coupling constants in Hz. Fast atom bombardment mass spectrometry (FAB-MS) (positive mode) (Micromass, Euroscience, Manchester, UK) analyses were performed using a Micromass Autospec M363 spectrometer. Open column chromatography (OCC) was carried out using packing materials of silica gel (Merck, Rahway, NJ, USA) and Sephadex LH-20 (Sigma, MO, USA). Vacuum liquid chromatography (VLC) was performed with macroporous resin D101. Eluents were collected using an SBS-160 fraction collector (Huxi Instrument Company, Shanghai, China). For thin layer chromatography (TLC), cellulose plates (25 DC-Plastikfolien Cellulose F, Merk) were used, with *t*-BuOH-HOAc-H_2O (3:1:1, v/v/v, solvent A) and HOAc-H_2O (3:47, v/v, solvent B) as the developing solutions. TLC spots were detected under UV light (365 and 254 nm) as well as by spraying with 1% $FeCl_3$ (in EtOH) reagent followed by heating. All solvents used in the extraction, isolation and separation were of analytical grade from Tianjin Liyuan Reagents Company, Tianjin, China.

Extraction, isolation and separation: Air-dried twig samples from *C. japonicum* (5.02 kg) were finely ground and then extracted with acetone:H_2O mixture (3:1, v/v) in a jar (25 l, 96 h each time) at room temperature for at least five times. As shown in Figure 1, after filtration and concentration in an evaporator under reduced pressure, the obtained raw extracts were suspended in H_2O and then subjected to a successive liquid-liquid fractionation with petroleum ether, *n*-hexane and chloroform in separation funnels. Then, the chloroform fraction was freeze-dried to obtain 56.92 g of $CHCl_3$ soluble fraction powders (labeled as TCJC) (yield 1.13%, w/w, on dry plant materials). As demonstrated in Figure 1, 45.66 g of fraction TCJC powders was subjected to VLC filled with macroporous adsorbent resin D101 using gradient washing solvents of MeOH:H_2O (49:1→19:1→4:1→1:4→1:19→1:49, v/v) to obtain five main portions ($TCJC_1$–$TCJC_5$). During the whole process, the eluents were monitored and grouped by TLC visualization. The portion $TCJC_3$ (15.36 g) was separated by silica gel OCC eluting with a gradient of decreasing $CHCl_3$ in EtOH (from 9:1 to 1:9, v/v) to yield five portions ($TCJC_{31}$–$TCJC_{35}$). The portion $TCJC_{32}$ (1.05 g) was purified by OCC filled with Sephadex LH-20 using MeOH:H_2O (4:1, 1:1, 1:3, v/v) as the washing solvent to obtain compound **I** (61.4 mg). The portion $TCJC_{34}$ (9.82 g) was successively loaded over silica gel and Sephadex LH-20 OCCs eluting with $CHCl_3$:MeOH (29:1→1:4, v/v) and MeOH:H_2O (3:1→1:7, v/v), respectively, to present 42.3 mg of compound **II** and 1.14 g of portion $TCJC_{3422}$. Compound **III** (59.6 mg) was obtained from $TCJC_{3422}$ by Sephadex LH-20 OCC washing with MeOH:H_2O (2:1→1:3, v/v). The main portion $TCJC_4$ (21.09) was also subjected to silica gel OCC using a step gradient of decreasing $CHCl_3$ in EtOH (from 19:1 to 1:4, v/v) to yield three portions ($TCJC_{41}$–$TCJC_{43}$). $TCJC_{42}$ (16.52 g) was also purified by silica gel OCC eluting with $CHCl_3$:MeOH (9:1→1:9, v/v) to give portion $TCJC_{421}$ and compound **IV** (70.6 mg). A total of 14.35 g of $TCJC_{421}$ was similarly applied to Sephadex LH-20 OCC with MeOH:H_2O (3:1, 1:1, 1:3, v/v) which acts as a mobile phase to yield compound **V** (47.2 mg) and 5.60 g of $TCJC_{4213}$. $TCJC_{4213}$ was further separated by Sephadex LH-20 OCC and sequentially eluted with MeOH:H_2O (4:1→1:5, v/v) and *n*-hexane:EtOH (2:1→1:4, v/v) to obtain compounds **VI** (54.0 mg) and **VII** (40.8 mg).

Table 1: NMR spectra data of compound **VII** in DMSO-d_6.

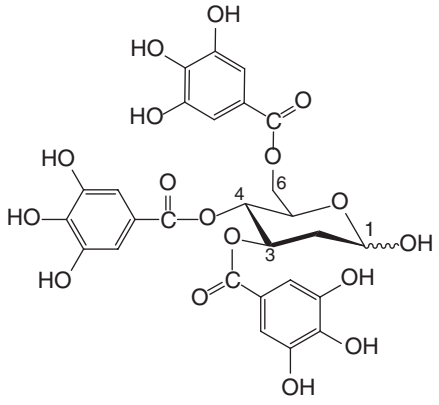
Position	^{1}H [m, *J* (Hz)]	^{13}C	DEPT
Aglycone moiety			
2	–	156.6	C
3	–	133.9	C
4	–	178.0	C
5	12.29 (1H, s, OH)	155.8	C
6	6.32 (1H, s)	99.7	CH
7	–	158.1	C
8	–	128.1	C
9	–	149.2	C
10	–	104.3	C
11-OCH_3	3.84 (3H, s)	60.9	CH_3
1′	–	123.0	C
2′/6′	8.12 (1H each, d, 8.9)	131.0	CH
3′/5′	7.09 (1H each, d, 8.9)	114.1	CH
4′	–	140.7	C
7′	–	165.7	C
Galloyl moiety			
1″	–	119.2	C
2″/6″	7.08 (1H each, s)	109.7	CH
3″/5″	–	146.3	C
4″	–	140.7	C
7″	–	165.7	C
Rhamnosyl moiety			
1‴	4.63 (1H, d, 1.5)	101.3	CH
2‴	3.81 (1H, m)	71.3	CH
3‴	3.45 (1H, m)	71.6	CH
4‴	3.27 (1H, m)	72.5	CH
5‴	3.13 (1H, m)	70.0	CH
6‴	1.01 (3H, d, 6.1)	17.9	CH_3

Compound VII: Yellowish amorphous powder; mp: 189–191°C; $[\alpha]_D^{20}$ –36.2° (MeOH, *c* 0.5); UV λ_{max} (nm) (MeOH): 223, 273, 322, 357; IR (KBr) ν_{max} cm^{-1} 3395 (OH), 1630 (α, β-unsaturated C=O), 1590, 1515, 1480 (aromatic C=C), 1165, 1065, 1020 (C-O); R_f: 0.20 (solvent A) and 0.77 (solvent B); FAB-MS (positive mode) data: found $[M+H]^+$ at *m/z* 615, $[M+Na]^+$ at *m/z* 637, and $[M+K]^+$ at *m/z* 653, coinciding with its molecular weight 614 and formula $C_{29}H_{26}O_{15}$; ^{1}H, ^{13}C and distortionless enhancement by polarization transfer (DEPT) NMR data are presented in Table 1; Selected heteronuclear multiple bond correlations (HMBCs) are shown in Figure 3.

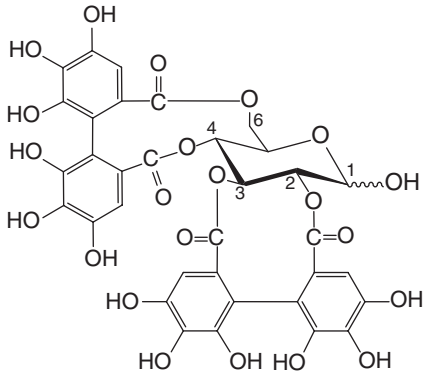
Results and discussion

Air-dried twigs of *C. japonicum* were extracted with 75% aqueous acetone to obtain the raw extracts. Successive liquid-liquid fractionations and repeated chromatographic purification of $CHCl_3$ soluble powders resulted in the isolation of a new galloylflavonol glycoside, elucidated as 8-methoxykaempferol-4′-*O*-galloyl-3-*O*-α-L-rhamnopyranoside (**VII**), as well as six known extractives, including three anomeric tannins (compounds **I** and **III**,

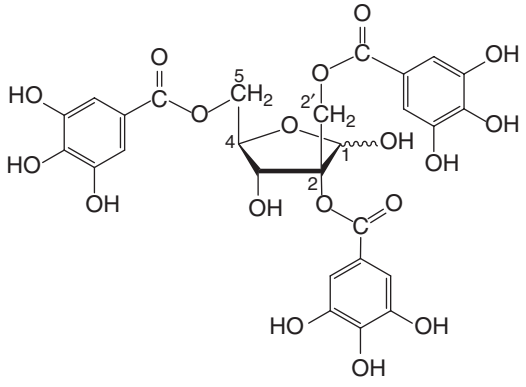
two anomeric galloyltannins; compound **II**, as an anomeric ellagitannin) and three flavonoids (compounds **IV**, **V** and **VI**). Based on their spectroscopic values and physicochemical clues, as well as by careful comparisons of the data with those reported in the literature, the six known extractives were determined as 3,4,6-tri-*O*-galloyl-β-D-glucopyranoside (**I**) (Haddock et al. 1982), pedunculagin (**II**) (Tanaka et al. 1993), 2,2′,5-tri-*O*-galloyl-α/β-D-hamamelose (**III**) (Lee et al. 2016), kaempferol-3-*O*-α-L-rhamnopyranoside (**IV**) (Harbone and Marby 1982), kaempferol (**V**) (Okuyama et al.



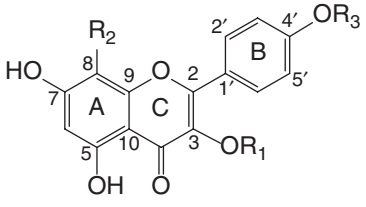
3,4,6-Tri-*O*-galloyl-β-D-glucopyranoside (**I**)



Pedunculagin (**II**)



2,2′,5-Tri-*O*-galloyl-α/β-D-hamamelose (**III**)



R_1 = α-L-rhamnosyl, R_2 = R_3 = H: Kaempferol-3-*O*-α-L-rhamnopyranoside (**IV**)

R_1 = R_2 = R_3 = H: Kaempferol (**V**)

R_1 = R_3 = H, R_2 = OMe: 8-Methoxykaempferol (**VI**)

R_1 = α-L-rhamnosyl, R_2 = OMe, R_3 = galloyl: 8-Methoxykaempferol-4′-*O*-galloyl-3-*O*-α-L-rhamnopyranoside (**VII**)

Figure 2: Structures of extractives **I** to **VII** isolated from the twigs of *C. japonicum*.

1978) and 8-methoxykaempferol (**VI**) (Dauguet et al. 1993) (as shown in Figure 2).

Among the six known compounds (**I**–**VI**), 2,2′,5-tri-*O*-galloyl-α/β-D-hamamelose (**III**) and kaempferol (**V**) were previously isolated from xylem and heartwood of *C. japonicum*, respectively (Lee et al. 2016). However, this was the first time that 3,4,6-tri-*O*-galloyl-β-D-glucopyranoside (**I**), pedunculagin (**II**), kaempferol-3-*O*-α-L-rhamnopyranoside (**IV**) and 8-methoxykaempferol (**VI**) were purified from the genus *Cercidiphyllum*.

Compound **VII** was obtained as a yellowish amorphous powder, with an mp of 189–191°C and optical rotation $[\alpha]_D^{20}$ –36.2° (*c* 0.5, in MeOH). The molecular formula of compound **VII** was determined to be $C_{29}H_{26}O_{15}$, for its positive FAB-MS spectrum displayed quasimolecular ion peaks $[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$ at *m/z* 615, 637 and 653, respectively, coinciding well with its molecular weight 614.

In TLC chromogenic reactions, when spraying with 1% ethanolic $FeCl_3$ solvent followed by heating, compound **VII** gave a dark brown color, accounting for the presence of one or more phenolic hydroxyl groups in its molecular structure. (Si et al. 2008). In two-dimensional (2D) TLC experiments, R_f values of compound **VII** were 0.20 and 0.77, when solvents A and B were used as the developing reagents, respectively. For compound **VII**, its IR spectrum presented characteristic absorption bands at 3395 cm^{-1} (OH), 1630 cm^{-1} (α, β-unsaturated C=O), 1590, 1515, 1480 cm^{-1} (aromatic C=C) and 1165, 1065, 1020 cm^{-1} (C-O) (Park et al. 2010; Hu et al. 2017). The UV spectrum of **VII** in MeOH exhibited absorption bands at λ_{max} 223, 273, 322 and 357 nm, corresponding with a 3-*O*-glycoside of 8-substitution flavonol skeleton (Dauguet et al. 1993; Koch et al. 2006).

The ^1H NMR spectrum of compound **VII** displayed a singlet at δ_H 12.29 which was attributable to a free hydroxyl group at C-5 of the A-ring. Another singlet observed at δ_H 6.32 was assigned to H-6 (Rayyan et al. 2005). A set of AA′BB′ coupling proton signals constituted by two doublets (J = 8.9 Hz) at δ_H 8.12 and 7.09 was assignable to H-2′, 6′ and H-3′, 5′ due to a *para*-substituted B-ring (Okoye et al. 2015). A methoxy group was recognized by its NMR evidence [δ_H 3.84 (3H, s), δ_C 60.9], and its linkage to C-8 was confirmed by ^1H detected HMBC experiment for $^1H \rightarrow {}^{13}C$ coupling correlation was observed between δ_H 3.84 (3H, s) of the OCH_3 and C-8 (δ_C 128.1) of the A-ring, as presented in Figure 3. In ^{13}C NMR spectrum of compound **VII**, characteristic flavonol signals resonated at δ_C 156.6 (C-2), 133.9 (C-3) and 178.0 (C-4). Thus, the aglycone was determined as a 8-methoxykaempferol (Dauguet et al. 1993).

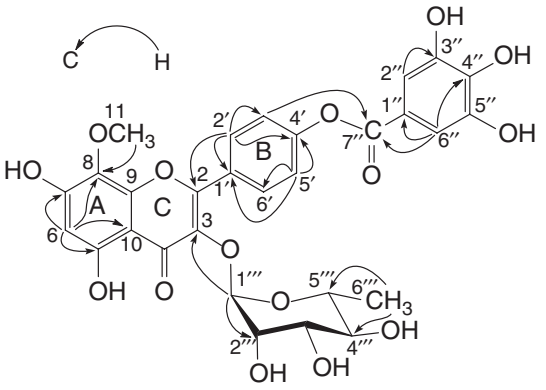


Figure 3: Key HMBC correlations observed in compound **VII**.

The presence of a galloyl moiety in compound **VII** was easily recognized from its ^1H NMR spectrum for a pair of symmetric protons H-2″ and H-6″ diagonally irradiating at δ_H 7.08 (1H each, s) (Si et al. 2016b). The HMBC spectroscopic correlations of **VII**, as demonstrated in Figure 3, presented interlinks between the aglycone B-ring proton H-3′/5′ (δ_H 7.09) and the quaternary carbon C-7″ (δ_C 165.7), which evidenced that the galloyl moiety was connected to C-4′ of the aglycone.

In the ^1H NMR spectrum of compound **VII**, the α-configuration of L-rhamnose was confirmed from a secondary methyl group characteristically irradiated at δ_H 1.01 (3H, d, J = 6.1 Hz, H-6‴) and an anomeric proton typically resonated at δ_H 4.63 (1H, d, J = 1.5) (Liu et al. 2017). In the ^{13}C NMR spectrum, the down-field shift of the C-2 signal (approximately Δ10 ppm) in compound **VII** compared with kaempferol (**V**) indicated that the glycosylation happened at 3-hydroxy of the aglycone (Dauguet et al. 1993). Moreover, the connection of α-L-rhamnosyl unit at C-3 of the 8-methoxykaempferol was also supported by the HMBC experiment of compound **VII**, in which the long-range coupling correlation was observed from H-1‴ (δ_H 4.63) of the rhamnosyl residue to C-3 (δ_C 133.9) (Okoye et al. 2015).

The combination of DEPT and ^{13}C NMR can distinguish the signals of different types of carbons. The detailed assignments for compound **VII** are illustrated in Table 1, where 29 carbon signals are sorted into 2 methyl, 12 methene, 12 methine and 15 tertiary carbons, while each carbon agrees well with the analyses presented above.

Consequently, compound **VII** was determined to be a galloylflavonol glycoside, and its chemical structure was elucidated as 8-methoxykaempferol-4′-*O*-galloyl-3-*O*-α-L-rhamnopyranoside, which is a new compound and has never previously been isolated from any other natural source.

Conclusions

The raw extracts from *C. japonicum* twigs are widely used in medicines to cure a variety of diseases or disorders. In this work, from the chloroform extracts of *C. japonicum* twigs, three anomeric tannins [3,4,6-tri-*O*-galloyl-β-D-glucopyranoside (**I**), pedunculagin (**II**), 2,2′,5-tri-*O*-galloyl-α/β-D-hamamelose (**III**)] and four flavonoids [kaempferol-3-*O*-α-L-rhamnopyranoside (**IV**), kaempferol (**V**), 8-methoxykaempferol (**VI**), and 8-methoxykaempferol-4′-*O*-galloyl-3-*O*-α-L-rhamnopyranoside (**VII**)] were purified and identified. The elucidation of the chemical structure of the compounds **I**–**VII** was achieved by their spectroscopic and chemical data. To date, **I**, **II**, **IV** and **VI** have not been isolated from the species of the *Cercidiphyllum* genus. Compound **VII** is a new galloylflavonol glycoside and its structure was elucidated for the first time in this work.

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Employment or leadership: None declared.
Honorarium: None declared.

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