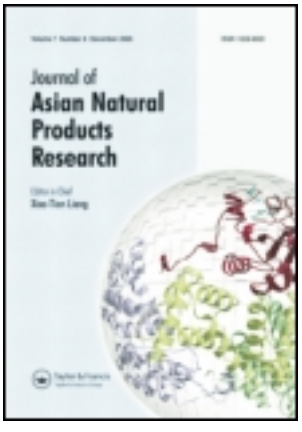

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Three new flavonoids from the active extract of *Fallopia convolvulus*

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Three new flavonoids from the active extract of *Fallopia convolvulus*

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Five solvent extracts (ethanol, petroleum ether, EtOAC, *n*-butanol, and water) from *Fallopia convolvulus* (L.) Löve were separated and their inhibitory effects on nitric oxide production in lipopolysaccharide-activated macrophages were evaluated. Three new flavonoids, falloconvolin A (**1**), falloconvolin B (**2**), and quercetin-3-*O*-(2-*E*-sinapoxyl)-glucopyranoside (**3**), together with 17 known phenolic compounds, were isolated from the active EtOAC extract, and their structures were elucidated on the basis of spectroscopic analysis and literature data.

Keywords: Polygonaceae; *Fallopia convolvulus*; flavonoids

1. Introduction

The genus *Fallopia* (Polygonaceae) is well known for producing pharmacologically active compounds and also for its use in oriental traditional medicine systems. The aqueous ethanolic extract of *Fallopia denticulata* possesses anti–inflammatory properties [1,2]. Additionally, compounds having anti–inflammatory, antibacteria, and antitumor activities have previously been isolated from *Fallopia multiflora* [3] and *F. multiflora* var. *ciliinerve* [4,5], respectively. The flavonoid and its glycosides from the methanolic extract of *Fallopia dumetorum*, *Fallopia dentate-alata*, and *Fallopia convolvulus* have been reported to show important chemotaxonomic status [6]. *F. convolvulus* (L.) Löve is an annual herb (1–1.5 m) indigenous to Gansu and is widely distributed in east-northern, west-northern part of China [7]. As one part of our ongoing phytochemical and bioactivity studies on Polygonaceae [4,5,8], the inhibitory effects on nitric oxide (NO) production in lipopolysaccharide (LPS)-activated macrophages of five solvent extracts (ethanol, petroleum ether, EtOAC, *n*-butanol, and water) from *F. convolvulus* were evaluated, and our investigation on the active EtOAC extract (ETE) resulted in the isolation of three new flavonoids **1**–**3**, together with 17 known compounds. Here, we describe the isolation and characterization of new compounds, and the inhibitory effects of extracts from *F. convolvulus* on NO production in LPS-activated macrophages (Figure 1).

2. Results and discussion

The air-dried aerial parts (10.1 kg) of *F. convolvulus* were extracted with 80% ethanol under reflux three times. The concentrated extract was suspended in H_2O and partitioned successively with petroleum ether, EtOAC, and *n*-BuOH to

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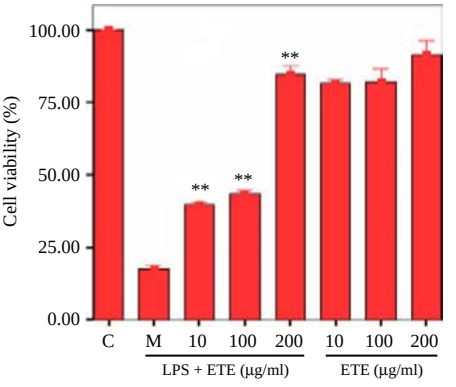

Figure 1. Cytotoxicity of ETE from *F. convolvulus* on RAW 264.7 cellls. C, control group; M, model group; $^{**}p < 0.01$ compared with model group.

afford five solvent extracts. Five solvent extracts (ethanol, petroleum ether, EtOAC, *n*-butanol, and water) were examined for their inhibitory effects on NO production induced by LPS in macrophages (see Table 1). Cell viability in the present experiment was determined by the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (MTT) method to find out whether the inhibition of NO production was due to cytotoxicity of the test sample (Figure 1). As shown in Table 1 and Figure 1, the ETE showed strong inhibition of NO production induced by LPS without cytotoxicity. After purification by repeated chromatography, the ETE afforded three new compounds **1**–**3**, whose structures were confirmed on the basis of spectroscopic analysis.

Compound **1** was obtained as a brownish yellow amorphous powder. The molecular formula $C_{17}H_{12}O_8$ of **1** was established from the quasi-molecular ion peaks at *m/z* 343.0509 $[M - H]^-$ in the HR-ESI-MS. The ^{1}H NMR spectrum of **1** exhibited *meta*-coupled aromatic signals at δ 6.17 (1H, d, $J = 1.8$ Hz, H-6) and 6.49 (1H, d, $J = 1.8$ Hz, H-8), and *ortho*-coupled aromatic signals at δ 6.65 (1H, d, $J = 8.2$ Hz, H-5′) and 6.88 (1H, d, $J = 8.2$ Hz, H-6′), and an aromatic proton signal at δ 6.55 (1H, s, H-3) except for one CH_2 at δ 3.35 (2H, s). The ^{13}C NMR spectrum of **1** exhibited 17 carbon signals, among which there are 14 carbon signals similar to luteolin except for one carbonyl (δ 174.0) and one CH_2 (δ 40.5) signals.

By extensive analysis of HMBC spectrum, some important correlations can be obtained as follows: from H-6′ to

Table 1. Inhibitory effects of different extracts from *F. convolvulus* on NO production induced by LPS in RAW 264.7 cells.

Samples	Dose (μg/ml)	NO production (μmol/l/10^5 cells)	Inhibitory rate (%)
Control		7.27 ± 0.01	
Models		59.48 ± 0.03[a]	
80% Ethanol extract	200	8.63 ± 0.01[b]	97.41
	100	25.57 ± 0.05[b]	59.56
	10	41.55 ± 0.08[b]	21.14
Petroleum ether extract	200	20.89 ± 0.02[b]	73.93
	100	22.73 ± 0.02[b]	66.40
	10	41.49 ± 0.04[b]	21.27
ETE	200	7.43 ± 0.01[b]	99.71
	100	8.65 ± 0.01[b]	97.65
	10	17.44 ± 0.01[b]	80.53
n-BuOH extract	200	7.98 ± 0.01[b]	98.65
	100	15.99 ± 0.01[b]	82.59
	10	46.43 ± 0.03[b]	9.40
L-NIL	50 μmol/l	50.08 ± 0.01[b]	35.2

Notes: [a] $p < 0.01$ compared with control group, [b] $p < 0.01$ compared with model group.

C-2 (166.1) and C-2′(123.6), from H-5′ to C-3′ (147.9) and C-1′ (122.6), from the CH_2 proton signal at δ 3.35 (2H, s) to C-2′ (123.6), C-1′ (122.6), C-3′ (147.9), and a carboxyl signal at δ 174.0 (C-7′), and this proved that the B ring of **1** was 2′,3′,4′-trisubstituted and the group of CH_2COOH was connected at C-2′ position. Therefore, the structure of **1** was deduced as 2-(6-(5,7-dihydroxy-4-oxo-4H-chromen-2-yl)-2,3-dihydroxyphenyl) acetic acid and named falloconvolin A (Figure 2).

Compound **2** was isolated as a yellow amorphous powder and the molecular formula $C_{26}H_{22}O_{10}$ was determined by the HR-ESI-MS at *m/z* 493.1151 $[M - H]^-$. The UV spectrum showed the typical characteristic of a flavonoid. In ^{1}H NMR and HSQC spectra, two *O*-methyl groups at δ 3.55 (6H, s, H-20 and 21), one oxygenated methylene at δ 3.24(1H, $J = 10.1$, 8.6 Hz, H-11a) and 3.37 (1H, $J = 10.1$, 6.1 Hz, H-11b), two aliphatic methine groups at δ 2.91(1H, dd, $J = 8.6$, 6.1 Hz, H-12) and 4.50 (1H, s, H-13), and six aromatic methine groups were observed. Among the six aromatic proton signals, the *meta*-coupled aromatic signals at δ 6.17 (1H, d, $J = 2.0$ Hz, H-6) and 6.45 (1H, d, $J = 2.0$ Hz, H-8) can be seen, which indicated that A ring of **2** may be 5,7-dihydroxy substituted, and the two aromatic signals at δ 6.29 (2H, s, H-15 and 19) indicated that **2** had a symmetric fragment.

In HMBC spectrum, H-13 showed nine long-range C—H correlations (with C-3, 12, and 14 via two bonds; with C-2, 4, 2′, 11, 15, and 19 via three bonds), whereas H-12 showed correlations with aromatic carbon signals of C-1′, 2′, 3′, 3, and 14, an aromatic signal of H-6′ at δ 7.39 (1H, s) showed correlations with C-2, 4′, and 2′; and another aromatic signal of H-3′ at δ 6.64 (1H, s) showed correlations with C-12, 1′, and 5′, which indicated that the B ring was 4′,5′-dihydroxy substituted. The complete assignment of proton and carbon resonances can be obtained by the analysis of HMBC and HSQC spectra, indicating compound **2** was a flavonolignan-type compound [9].

The relative stereochemistry at the benzylic positions is *cis* in view of the singlet nature of the signal at δ 4.50 due to H-13. This indicates that H-12 and H-13 are not diaxially oriented. In ^{1}H NMR spectrum, H-11a (3.24, $J = 10.1$, 8.6 Hz), H-11b (3.37, dd, $J = 10.1$, 6.1 Hz), and H-12 (2.91, dd, $J = 8.6$, 6.1 Hz) both resonated as double doublets, whereas H-13 appeared as a sharp singlet. From these findings, an axial orientation of H-13 and an equatorial orientation of H-12 were deduced. Compound **2** gave a negative $[\alpha]_D$ value. These relative structures are also similar to those of a known flavonolignan, whose absolute configuration was 12*S*, 13*S* [10]. So, the structure of **2** was deduced as 12,13-dihydro-3′,4′,5,7-tetrahydroxy-12-hydroxymethyl-13-(17-hydroxyl-16,18-dimethoxyphenyl)-7*H*-benzo[*c*]xanthen-4-

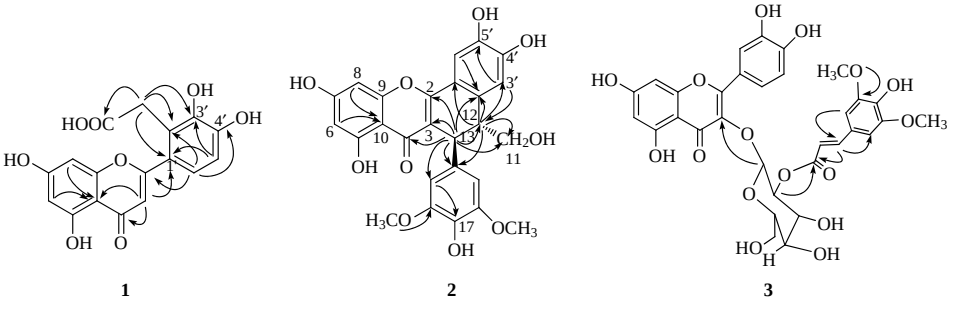

Figure 2. Key HMBC correlations of compounds **1**–**3**.

one and named as falloconvolin B (**2**) (Figure 2).

Compound **3** was obtained as a yellow amorphous powder, and its molecular formula $C_{32}H_{30}O_{16}$ was determined on the basis of HR-ESI-MS at *m/z* 669.1437 $[M - H]^-$. The IR spectrum showed absorptions for hydroxyl groups (3451 cm^{-1}) and carbonyl group (1630 cm^{-1}). The ^1H and ^{13}C NMR and HSQC spectra of **3** suggested the presence of an aglycone of quercetin with five aromatic proton signals at δ 7.60 (1H, d, $J = 1.8$ Hz, H-2′), 6.85 (1H, d, $J = 8.6$ Hz, H-5′), 7.52 (1H, dd, $J = 8.6$, 1.8 Hz, H-6′), 6.36 (1H, d, $J = 1.2$ Hz, H-8), and 6.16 (1H, d, $J = 1.2$ Hz, H-6), one glucosyl moiety with a sugar H-1 doublet (δ $J = 7.8$ Hz) and a *trans*-sinapoyl moiety. In HMBC spectrum, the proton signals of H-2′ and 6′ also showed correlations with C-2 (δ 156.4). The site of glucose attached to quercetin was considered to be 3-hydroxyl group by the chemical shift of H-1″ at δ 5.76 [11] and by comparison with the NMR spectral data of quercetin-3-*O*-β-D-glucoside [12]. The sinapoyl residue is shown to be attached to 2-hydroxy of glucose by the downfield chemical shift of H-1″ from δ 4.88 in quercetin-3-*O*-quercetin to δ 5.76 (H-1″). Comparison of the NMR spectral data for **3** with those of 7-*O*-methyl herbacetin-3-*O*-β-(2-*O*-*E*-feruloyl)-D-glucoside [11] also showed that **3** had a sinapoyl residue attached to 2-hydroxyl of glucose. The correlation from H-2″ to the carbonyl signal at δ 165.9 (C-9‴) in HMBC spectrum can also be obtained. So, compound **3** is assigned to be quercetin-3-*O*-(2-*E*-sinapoyl)-glucopyranoside (Figure 2).

In addition to three new flavonoids **1**–**3**, 17 known compounds, namely, 5″-methoxyhydnocarpin (**4**) [13], quercetin-3-*O*-β-D-glucoside (**5**) [12], philonotisflavone (**6**) [14], emodin (**7**), physcion (**8**), frangulin A (**9**) [15], endocrocin (**10**) [16], laccaic acid (**11**) [17], emodin-8-*O*-β-D-glucoside (**12**) [17], physcion-8-*O*-β-D-glucoside (**13**) [17], caffeoylcolic acid (**14**) [18], methyl caffeoylglycolate (**15**) [18], caffeic acid (**16**) [19], *p*-coumaroyl-glucoside (**17**) [20], ferulic acid (**18**), ferulic acid tetracosyl ester (**19**) [21], and isoferulic acid tetracosyl ester (**20**) [22] were also isolated and identified by comparison of their spectroscopic data with those reported in the literature or comparing with the reference compound in TLC. Among the isolated ones, there are two flavonolignans, namely falloconvolin B (**2**) and 5″-methoxyhydnocarpin (**4**).

NO was shown to be involved in physiological processes, such as chronic or acute inflammation, that is produced by the oxidation of L-arginine by NO synthase (NOS). NOS is involved in a pathological aspect with the overproduction of NO, and can be expressed in response to pro-inflammatory agents [23]. The herbs of *F. convolvulus* as folklore medicine possess anti-inflammatory properties, and the inhibitory effects of its five solvent extracts (ethanol, petroleum ether, EtOAC, *n*-butanol, and water) on NO production in LPS-activated macrophages were evaluated. ETE showed the strongest suppressing action on NO formation. In a previous paper, the compatibility of anthraquinone and total flavonoids of Xie-xin decoction showed no obvious influence on the growth activity of macrophage, but obviously inhibited the NO production [24], and compounds aloe-emodin and flavonoids with double bond between C-2 and C-3 positions showed inhibitory effect on NO production [25,26]. So, these isolated compounds in this paper may be an important evidence substantiating the traditional effects of this herbal medicine for the treatment of inflammation by inhibiting NO production.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a Buchi apparatus and were uncorrected. Optical rotations were measured with a JASCO P-1020 digital automatic polarimeter. The

UV spectra were recorded on a Shimadzu UV-2501 spectrometer (Kyoto, Japan). IR spectra were recorded on a Nicolet Impact 410 infrared spectrophotometer (Madison, WI, USA). HR-ESI-MS were obtained on an Agilent G3250AA LC/MSD TOF mass spectrometer (Santa Clara, CA, USA). NMR experiments were performed on a Brucker AV-300 spectrometer (Fallanden, Switzerland) with TMS as the internal standard. Silica gel (200–300 mesh for column chromatography (CC) and GF_{254} for TLC) was obtained from Qingdao Marine Chemical Company (Qingdao, China). Sephadex LH-20 was obtained from Amersham Biosciences (Uppsala, Sweden).

3.2 Plant material

F. convolvulus (L.) Löve were collected in Lanzhou County, Gansu Province, China, in August 2008. The plant was identified by Prof. Mian Zhang of China Pharmaceutical University. A voucher specimen (No. FC-08-08) has been deposited in the Research Department of Pharmacognosy, China Pharmaceutical University.

3.3 Extraction and isolation

The air-dried aerial parts of *F. convolvulus* (10.1 kg) were extracted with 80% ethanol under reflux three times. The solvent was removed under reduced pressure to yield crude extract (1.9 kg). The crude extract was suspended in water and fractionated by successive partitioning with petroleum ether, EtOAC, and *n*-BuOH, respectively. The EtOAC portion (355 g) was chromatographed on a silica gel column using stepwise elution with petroleum ether–EtOAC (100:1, 50:1, 20:1, 10:1, and 1:1) to give 18 fractions (Fraction A–Fraction R). Fraction C (1.0 g) and H (0.5 g) gave **7** (3 mg) and **8** (2 mg), respectively, after purification by two CC (SiO_2: petroleum ether–EtOAC (15:1) and Sephadex LH-20: $CHCl_3$–MeOH (1:1)). Fraction F (2.5 g) gave **19** (8 mg) and **20** (25 mg) by repeated purification on silica gel column with EtOAC–MeOH (10:1, 5:1, and 2:1). Fraction L (5.1 g) was subjected to silica gel column with $CHCl_3$–MeOH (3:1) and purified through Sephadex LH-20 with $CHCl_3$–MeOH (1:1) to give **14** (15 mg), **16** (5 mg), and **18** (10 mg). Fraction N (10 g) was retreated on silica gel column and eluted with $CHCl_3$–MeOH–formic acid mixtures (50:1:0.5, 15:1:0.5, 10:1:0.5, 3:1:0.5, and 1:1:0.5) to give three sub-fractions (Fraction NA (3.2 g), Fraction NB (0.8 g), and Fraction NC (1.4 g)); Fraction NA was retreated on silica gel CC, eluted with CH_2Cl_2–MeOH–H_2O (15:1:1), and finally reapplied to a Sephadex LH-20 column using MeOH to yield compounds **1** (20 mg) and **2** (25 mg); Fraction NB was retreated on Sephadex LH-20 CC and eluted with $CHCl_3$–MeOH (1:1) to give **15** (18 mg); and Fraction NC was repeatedly subjected to silica gel CC (EtOAC–MeOH, 10:1) to give **3** (10 mg). Fraction O (5.8 g) was put on silica gel column with $CHCl_3$–MeOH (10:1, 2:1, and 1:2) to give two sub-fractions (Fraction OA (2.1 g) and Fraction OB (1.0 g)); Fraction OA was then purified by Sephadex LH-20 with MeOH to give **6** (4 mg) and **9** (6 mg); and Fraction OB was retreated on Sephadex LH-20 column with $CHCl_3$–MeOH (1:1) to give **10** (13 mg). Fraction Q (30 g) was subjected to silica gel CC using $CHCl_3$–MeOH–formic acid mixtures (8:1:0.05, 4:1:0.05, 2:1:0.05, and 1:1:0.05) to give five sub-fractions (Fraction QA–fraction QE). Fraction QA (5.1 g) was purified on Sephadex LH-20 with $CHCl_3$–MeOH (1:1) to give **17** (30 mg); Fraction QB (6.3 g) was retreated repeatedly on silica gel column with $CHCl_3$–MeOH (5:1) to give **4** (15 mg) and **5** (22 mg); and Fraction QD (7.2 g) was retreated on silica gel column with $CHCl_3$–acetone (5:1, 3:1, and 1:1), and then purified in a Sephadex LH-20 column using MeOH to give **11** (4 mg), **12** (8 mg), and **13** (4 mg).

*3.3.1 2-(6-(5,7-Dihydroxy-4-oxo-4H-chromen-2-yl)-2,3-dihydroxyphenyl) acetic acid (**1**)*

Brownish yellow amorphous powder (MeOH). mp. 285–286°C. IR ν_{max} (KBr): 3442, 1629, 1630, 1121 cm^{-1}. UV(MeOH) λ_{max} (nm) (log ε): 332 (3.33), 293 (3.42), 260 (4.58). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 12.99 (1H, s, 5-OH), 6.55 (1H, s, H-3), 6.17 (1H, d, $J = 1.8$ Hz, H-6), 6.49 (1H, d, $J = 1.8$ Hz, H-8), 6.65 (1H, d, $J = 8.2$ Hz, H-5′), 6.88 (1H, d, $J = 8.2$ Hz, H-6′), 3.35 (2H, s, CH_2). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 166.1 (C-2), 103.3 (C-3), 181.5 (C-4), 161.2 (C-5), 98.6 (C-6), 163.9 (C-7), 94.2 (C-8), 157.9 (C-9), 103.5 (C-10), 122.6 (C-1′), 123.6 (C-2′), 147.9 (C-3′), 149.6 (C-4′), 112.3 (C-5′), 118.8 (C-6′), 174.0 (C-7′), 40.5 (C-8′). Negative ion ESI-MS *m/z*: 343.0 $[M - H]^-$. HR-ESI-MS *m/z*: 343.0509 $[M - H]^-$ (calcd for $C_{17}H_{11}O_8$, 343.0454).

*3.3.2 12,13-Dihydro-3′,4′,5,7-tetrahydroxy-12-hydroxymethyl-13-(17-hydroxyl-16,18-dimethoxyphenyl)-7H-benzo[c]xanthen-4-one (**2**)*

Yellow powder (MeOH). mp. 203–204°C. $[\alpha]_D^{25}$ −20.5 ($c = 0.1$, MeOH). IR ν_{max} (KBr): 3450, 1656, 1620, 1517, 1373, 1310, 1112 cm^{-1}. UV(MeOH) λ_{max} (nm) (log ε): 374 (4.55), 260 (sh, 4.65), 226 (4.73). ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 13.06 (1H, s, 5-OH), 6.17 (1H, d, $J = 2.0$ Hz, H-6), 6.45 (1H, d, $J = 2.0$ Hz, H-8), 3.24 (1H, $J = 10.1$, 8.6 Hz, H-11a), 3.37 (1H, $J = 10.1$, 6.1 Hz, H-11e), 2.91 (1H, dd, $J = 8.6$, 6.1 Hz, H-12), 4.50 (1H, s, H-13), 6.29 (2H, s, H-15, 19), 3.55 (6H, s, H-20, 21), 6.64 (1H, s, H-3′), 7.39 (1H, s, H-6′). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 158.6 (C-2), 133.3 (C-3), 180.3 (C-4), 161.6 (C-5), 98.8 (C-6), 163.9 (C-7), 93.8 (C-8), 156.8 (C-9), 103.8 (C-10), 64.7 (C-11), 48.7 (C-12), 35.1 (C-13), 112.4 (C-14), 105.0 (C-15, 19), 147.8 (C-16, 18), 134.6 (C-17), 56.0 ($2 \times OCH_3$), 117.6 (C-1′), 131.6 (C-2′), 117.1 (C-3′), 149.6 (C-4′), 144.8 (C-5′), 110.9 (C-6′). Negative ion ESI-MS *m/z*: 493.1 $[M - H]^-$, positive ion ESI-MS *m/z*: 495.1 $[M + H]^+$. HR-ESI-MS *m/z*: 493.1151 $[M - H]^-$ (calcd for $C_{26}H_{21}O_{10}$, 493.1140).

*3.3.3 Quercetin-3-(2-E-sinapoyl)-O-glucopyranoside (**3**)*

Yellow powder (MeOH). mp. 205–206°C. $[\alpha]_D^{25}$ −180.3 ($c = 0.4$, Pyridine). IR ν_{max} (KBr): 3451, 1714, 1630, 1518, 1366, 1291, 1116 cm^{-1}. UV(MeOH) λ_{max} (nm) (log ε): 337.4 (4.08), 245 (sh, 4.07), 205 (4.47). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 6.16 (1H, d, $J = 1.2$ Hz, H-6), 6.36 (1H, d, $J = 1.2$ Hz, H-8), 7.60 (1H, d, $J = 1.8$ Hz, H-2′), 6.85 (1H, d, $J = 8.6$ Hz, H-5′), 7.52 (1H, dd, $J = 1.8$, 8.6 Hz, H-6′), 5.75 (1H, d, $J = 8.0$ Hz, H-1″), 7.00 (1H, s, H-2‴, 6‴), 6.53 (1H, d, $J = 15.9$ Hz, H-7‴), 7.58 (1H, d, $J = 15.9$ Hz, H-8‴), 3.80 (6H, s, H-10‴, 11‴). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 156.4 (C-2), 138.4 (C-3), 177.3 (C-4), 161.4 (C-5), 98.8 (C-6), 164.3 (C-7), 93.6 (C-8), 156.3 (C-9), 104.1 (C-10), 121.1 (C-1′), 115.4 (C-2′), 145.0 (C-3′), 148.7 (C-4′), 116.1 (C-5′), 122.1 (C-6′), 98.4 (C-1″), 74.4 (C-2″), 74.2 (C-3″), 70.3 (C-4″), 78.0 (C-5″), 60.9 (C-6″), 124.6 (C-1‴), 106.3 (C-2‴, 6‴), 148.2 (C-3‴, 5‴), 144.7 (C-4‴), 115.3 (C-7‴), 145.7 (C-8‴), 165.9 (C-9‴), 56.2 (C-10‴, 11‴). Negative ion ESI-MS *m/z*: 669.1 $[M - H]^-$. HR-ESI-MS *m/z*: 669.1437 $[M - H]^-$ (calcd for $C_{32}H_{29}O_{16}$, 669.1456).

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