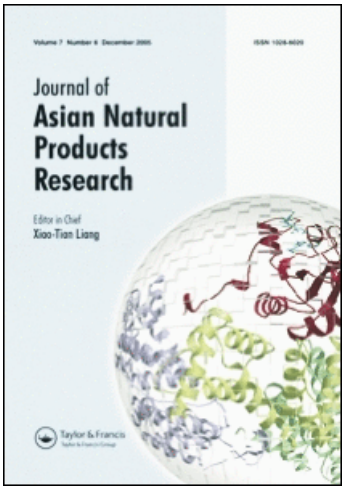

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CHEMICAL CONSTITUENTS OF *PYRROSIA PETIOLOSA*

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This paper is dedicated to Professor Xiao-Tian Liang on the occasion of his 80th birthday.

The new flavone diglycoside 7-*O*-[6-*O*-(α-L-arabifuranosyl)-β-D-glucopyranosyl]-gossypetin, named as pyrropetioside, along with 13 known compounds (including 3 artifacts) have been isolated from *Pyrrosia petiolosa*. Their structures have been elucidated by means of chemical and spectroscopic methods including IR, MS, 1D and 2D NMR techniques.

Keywords: *Pyrrosia petiolosa*; Flavone diglycoside; Pyrropetioside A; Chromatography

INTRODUCTION

In the Chinese Pharmacopoeia, three *Pyrrosia* species, *P. lingua*, *P. sheareri* and *P. petiolosa*, are used as sources of the Chinese traditional remedy "Shiwei" which is used for the treatment of swelling, urocystitis, urinary calculus, bloody urine, coughs and bronchitis, *etc.* [1,2]. *Pyrrosia petiolosa* was found to be the most commonly used in the investigation of Chinese markets in 16 cities. To determine the indicative of components and to control its quality by a HPLC fingerprint technique, we carried out a systematic study of chemical constituents of *P. petiolosa*. Previously only a few usual metabolites have been reported from this plant [3]. From the ethanolic extract 14 compounds have been isolated and studied by chemical and spectroscopic methods, including IR, MS, 1D and 2D NMR techniques. Their structures (Fig. 1) were identified as 7-*O*-[6-*O*-(α-L-arabifuranosyl)-β-D-glucopyranosyl]-gossypetin (**1**), gossypetin 3,8-di-*O*-β-D-glucopyranoside (**2**) [4], gossypetin 7-*O*-β-D-glucopyranoside (**3**) [5], herbacetin 7-*O*-β-D-glucopyranoside (**4**) [6], astragalin (**5**), kaempferol 3,7-di-*O*-β-D-glucopyranoside (**6**) [7], (±)-eriodictyol 7-*O*-β-D-pyranoglucuronide (**7**), (±)-eriodictyol 7-*O*-β-*D*-pyranoglucuronide methyl ester (**8**) [8], (±)-eriodictyol 7-*O*-β-D-pyranoglucuronide ethyl ester (**9**), chlorogenic acid (**10**), methyl chlorogenate (**11**) [9–11], (−)-eriodictyol (**12**), kaempferol (**13**), naringenin (**14**) [12], and a large amount of sucrose. Among them compound **1**, named pyrropetioside A, is a new flavone diglycoside, and **8**, **9** and **11** were found to be artifacts. Except for chlorogenic acid (**10**) and sucrose,

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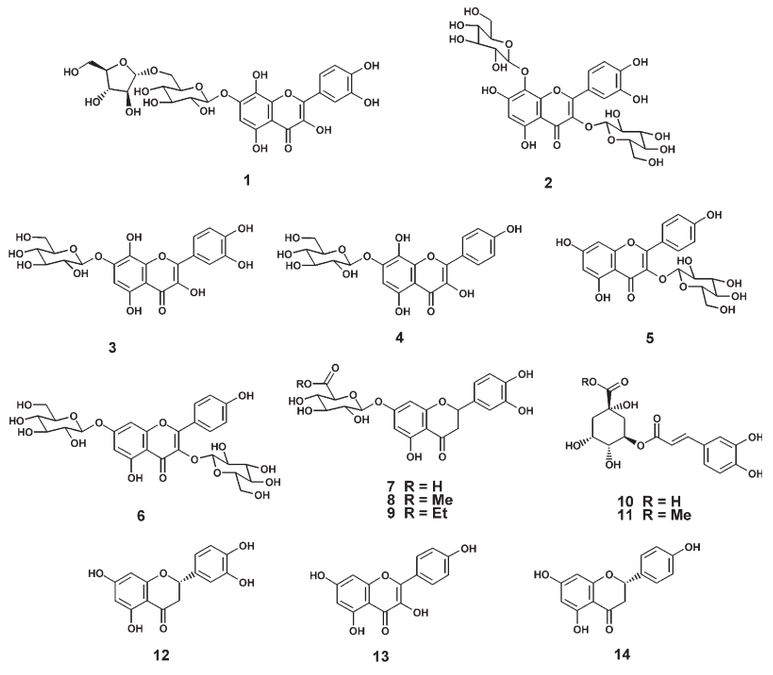

FIGURE 1 Structures of compounds **1**–**14**.

the other compounds were isolated from this plant for the first time. Compound **7** is the most abundant in this plant. In the HPLC quantitative analyses of 12 samples of this plant collected in 16 cities of China, the amount of compound **6** is 0.861–2.743%.

RESULTS AND DISCUSSION

Compound **1** was obtained as a yellow powder, mp 188–190°C, $[\alpha]_D^{22}$ −56.0 (*c* 0.20, MeOH). Its IR spectrum (KBr) showed absorption bands for hydroxyl (3388 cm^{-1}), conjugated carbonyl (1658 cm^{-1}) groups and aromatic rings (1614 and 1514 cm^{-1}). The FABMS spectrum exhibited a quasi-molecular ion peak at *m/z* 613 $[M + H]^+$, and the molecular formula was determined as $C_{26}H_{28}O_{17}$ by HRFABMS at *m/z* 613.1418. The ^1H NMR spectrum of **1** in DMSO showed signals assigned to a 1,3,4-trisubstituted phenyl moiety at δ 7.74 (1H, d, $J = 1.8$ Hz, 2′ − H), 7.61 (1H, dd, $J = 8.7$ and 1.8 Hz, 6′-H), 6.88 (1H, d, $J = 8.7$ Hz, 5′-H), an isolated aromatic proton at δ 6.62 (1H, s, 6-H), and five exchangeable phenolic hydroxyl protons at δ 11.88 (1H, s, 5-OH), 9.60 (1H, s, 3′-OH), 9.42 (1H, s, 3-OH), 9.32 (1H, s, 4′-OH) and 8.57 (1H, s, 8-OH), as well as signals attributed to two anomeric protons at δ 4.81 (1H, d, $J = 7.2$ Hz, 1″-H) and 4.72 (1H, s, 1‴-H) together with 11 glycosyl protons in the range δ 3.9–3.1. The ^{13}C NMR and DEPT spectra of **1** displayed 26 carbon signals consisted of 15 sp^2 carbons of a flavone aglycone and 11 sp^3 carbons of two glycosyl moieties (see Table I). All of the above data revealed that **1** is a flavone diglycoside with an α sugar and a β sugar unit. The signals in the ^1H and ^{13}C NMR spectra were unambiguously assigned by HMQC and HMBC experiments. The signals assigned to the aglycon moiety were in good agreement with those of gossypetin [13]. Signals assigned to sugar units revealed the presence of a terminal α-L-arabifuranosyl unit and a 6-substituted

TABLE I ^{1}H and ^{13}C NMR data of compound **1***

Aglycone moiety			*Sugar moiety*		
No.	δ_H	δ_C	*No.*	δ_H	δ_C
2		147.2	1″	4.81 d (7.2)	101.2
3		135.6	2″	3.38 m	73.2
4		176.1	3″	3.60 m	75.6
5		151.3	4″	3.15 dd (7.8, 7.5)	69.9
6	6.62 s	97.8	5″	3.57 m	75.4
7		150.1	6″	3.91 br d (10.2)	67.0
8		126.6		3.40 dd (10.2, 7.8)	
9		143.8	1‴	4.72 s	108.5
10		104.6	2‴	3.77 m	81.9
1′		122.0	3‴	3.62 m	77.1
2′	7.74 d (1.8)	115.4	4‴	3.72 m	83.8
3′		144.9	5‴	3.53 m	61.2
4′		147.7		3.36 m	
5′	6.88 d (8.7)	115.1			
6′	7.61 dd (8.7, 1.8)	120.1			

* NMR data were measured in DMSO at 500 MHz for proton and at 125 MHz for ^{13}C. Proton coupling constants (J) in Hz are given in parenthesis. The assignments were based on DEPT, $^{1}H-^{1}H$ COSY, HMQC and HMBC experiments.

β-D-glucopyranosyl unit [14,15]. After acidic hydrolysis of **1** the Co-TLC and Co-PC confirmed the released arabinose and glucose from **1**. In the HMBC spectrum (see Fig. 2) long-range correlations from H-1″ to C-7 and H-1″ to C-6″ unequivocally established that a disaccharide α-L-arabifuranosyl (1 → 6)-β-D-glucopyranosyl moiety was located at C-7 of the aglycon. Accordingly, the structure of **1** was determined as 7-*O*-[6-*O*-(α-L-arabifuranosyl)-β-D-glucopyranosyl]-gossypetin.

Compounds **8**, **9** and **11** were not detected by HPLC in the extract. However, when **7** was kept in MeOH at room temperature (26°C) for 6 h and refluxed in EtOH at 60°C for 8 h, **8** and **9** were not only detected by HPLC but also isolated by chromatography over silica gel using $CHCl_3$–MeCN (5:1) from the solutions in yields of 17% and 4%, respectively. Compound **10** could be converted into **11** with a yield of 31% by keeping it in MeOH at room temperature (26°C) for 12 h. Therefore, **8**, **9** and **11** are artifacts of the extraction and isolation procedure.

EXPERIMENTAL

General Procedures

Melting points were determined on an XT-4 micro melting point apparatus and are uncorrected. Optical rotations were measured on a Rudolph Research Autopol III automatic

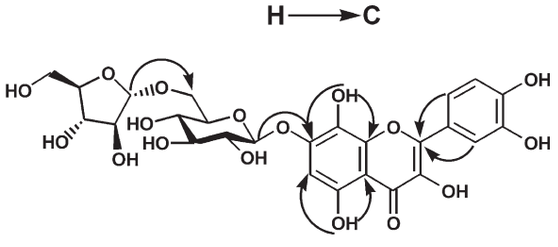

FIGURE 2 Key HMBC correlations of **1**.

polarimeter. UV spectra were measured on a Shumazu UV-260 instrument. IR spectra were recorded as KBr disks on a Nicolet Impact 400 FT-IR instrument. NMR spectra were recorded on Varian Mercury-300 and Inova 500 MHz spectrometers in DMSO-d_6 or acetone-d_6 with TMS as internal standard. EIMS, FABMS and HRFABMS data were obtained with a Micromass Autospec-Ultima ETOF spectrometer. Column Chromatography was performed with RA macro porous resin (Beijing Seventh Chemical Inc., China), silica gel (200–300 mesh, Qingdao Marine Chemical Inc. China), RP-18 reverse phase silica gel (43–60 μm) and Sephadex LH-20 (Pharmacia Biotech AB, Uppsala Sweden). TLC was carried out with glass precoated silica gel GF_{254} plates. Spots were visualized under UV light and by spraying with 7% H_2SO_4 in 95% EtOH followed by heating. All solvents used either were spectral grade or were distilled prior to use.

Plant Material

Leaves of *Pyrrosia petiolosa* were collected in Huairou district of Beijing, China in September 2000. Plant identification was verified by Professor Wanzhi Song (Department of Medicinal Plants, Institute of Materia Medica, Beijing 100050, China). Voucher specimens (No. 200026) were deposited at the Herbarium of the Department of Medicinal Plants, Institute of Materia Medica.

Extraction and Isolation

Air-dried and grounded leaves of *Pyrrosia petiolosa* (15.8 kg) were extracted with EtOH at room temperature (3 × 24 h), and the solvent was removed under reduced pressure at $< 40°C$ to give a residue (1657 g). The residue was suspended in water and then partitioned with EtOAc. After evaporation under vacuum to remove the remaining EtOAc, the water phase was subjected to column chromatography over RA resin, eluting with H_2O and EtOH successively. The water eluted solution was concentrated, and the residue was dissolved in 90% MeOH. After storing the solution for several days a large amount of sucrose (598 g) was obtained as prism crystals. The EtOH eluted solution was concentrated to give a residue (273 g) that was chromatographed over silica gel (800 g) eluting with $CHCl_3$–MeOH (80:1–0:1 gradient), and separated into 18 fractions (I-XVIII) on the basis of TLC analyses. Subsequent purifications of fractions III, IV and VI by column chromatography over Sephadex LH-20 eluting with $CHCl_3$–MeOH (5:1), afforded naringenin (**14**) (7 mg), (−)-eriodictyol (**12**) (72 mg) and kaempferol (**13**) (103 mg), respectively. Fraction VIII was separated into three subfractions by column chromatography over Sephadex LH-20, eluting with $CHCl_3$–MeOH (5:1). The third fraction was repeatedly purified by column chromatography over reverse-phase silica gel (RP-18), eluting with a gradient increasing in acetonitrile (0–100%) in H_2O to yield (±)-eriodictyol 7-*O*-β-D-pyranoglucuronide (**7**) (2469 mg), (±)-eriodictyol 7-*O*-β-D-pyranoglucuronide methyl ester (**8**) (1647 mg), (±)-eriodictyol 7-*O*-β-D-pyranoglucuronide ethyl ester (**9**) (71 mg), chlorogenic acid (**10**) (1772 mg), methyl chlorogenate (**11**) (2112 mg). Fraction XI was purified by column chromatography over Sephadex LH-20 using $CHCl_3$–MeOH (3:1) as eluent to yield 7-*O*-[6-*O*-(α-L-arabifuranosyl)-β-D-glucopyranosyl]-gossypetin (**1**) (92 mg) and gossypetin 7-*O*-β-D-glucopyranoside (**3**) (711 mg). Fraction XII was separated into three subfractions by chromatography over Sephadex LH-20 using $CHCl_3$–MeOH (3:1) as eluent. The third fraction was further purified by column chromatography over silica gel, eluting with $CHCl_3$–MeOH (3:1), to obtain astragalin (**5**) (83 mg) and herbacetin 7-*O*-β-*D*-glucopyranoside (**4**) (24 mg). Fraction XIII was separated into two subfractions by chromatography over Sephadex LH-20 using $CHCl_3$–MeOH (3:1) as eluent. The second fraction was purified by

column chromatography over silica gel using $CHCl_3$–MeOH–H_2O (2.5:1:0.1) as eluent to yield gossypetin 3,8-di-*O*-β-D-glucopyranoside (**2**) (14 mg) and kaempferol 3,7-di-*O*-β-D-glucopyranoside (**6**) (29 mg).

7-O-[6-O-(α-L-Arabifuranosyl)-β-D-glucopyranosyl]-gossypetin (1)

A yellow amorphous powder, mp 189–190°C, $[\alpha]_D^{22}$ −56.0 (*c* 0.20, MeOH); UV (MeOH) λ_{max} (ϵ) 204 (2.53×10^4), 262 (1.29×10^4), 277 (sh, 1.02×10^4), 346 (7.1×10^3), 358 (7.4×10^3), 389 (8.5×10^3) nm; IR(KBr) ν_{max} 3388, 2933, 1658, 1614, 1566, 1514, 1450, 1354, 1319, 1261, 1072, 997, 978, 951, 901, 816, 789 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) and ^{13}C NMR (DMSO-d_6, 125 MHz) see Table I. FABMS *m/z*: 613 $[M + H]^+$; HRFABMS *m/z* 613.1418 (calcd for $C_{26}H_{29}O_{17}$ 613.1405).

Acidic Hydrolysis of 1

Compound **1** (32 mg) was refluxed with 10% H_2SO_4 (10 ml) for 8 h at 94°C. After the reaction solution was cooled, a yellow precipitate was obtained by filtration. The precipitate was chromatographed over Sephadex LH-20, eluting with $CHCl_3$–MeOH (5:1), to yield the aglycone (6.4 mg). The aglycone was identified as gossypetin by comparison of its spectral data with those reported in literature[4]. After neutralization with $BaCO_3$, the aqueous filtrate was concentrated and then subjected to TLC and PC together with authentic arabinose and glucose samples, which clearly indicated that they existed in the solution. The developing solvent systems were $CHCl_3$–MeOH (2.5:1) for TLC and the upper layer of *n*-BuOH–AcOH–H_2O (4:1:5) for PC, and the spots were colored by spraying aniline hydrogen phthalate followed by heating at 105°C.

Gossypetin 3,8-di-O-β-D-glucopyranoside (2)

A yellow amorphous powder; ^1H NMR (DMSO-d_6, 500 MHz) δ 12.49 (1H, s, 5-OH), 10.65 (1H, s, 7-OH), 9.66 (1H, s, 3′-OH), 9.19 (1H, s, 4′-OH), 7.82 (1H, dd, $J = 8.4$ and 2.4 Hz, 6′-H), 7.80 (1H, d, $J = 2.4$ Hz, 2′-H), 6.84 (1H, d, $J = 8.4$ Hz, 5′-H), 6.26 (1H, s, 6-H), 5.49 (1H, d, $J = 7.2$ Hz, 1″-H), 4.65 (1H, d, $J = 7.8$ Hz, 1‴-H), 3.7–3.1 (12H, m, glu-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 178.2 (C-4), 157.6 (C-5), 157.2 (C-7), 157.0 (C-2), 149.3 (C-9), 149.1 (C-4′), 145.2 (C-3′), 133.9 (C-3), 125.7 (C-8), 123.1 (C-6′), 121.8 (C-1′), 117.4 (C-2′), 115.9 (C-5′), 107.0 (C-1‴), 104.5 (C-10), 101.5 (C-1″), 99.5 (C-6), 78.4 (C-3‴), 77.8 (C-3″), 77.2 (C-5‴), 76.6 (C-5″), 74.7 (C-2‴), 74.6 (C-2″), 70.6 (C-4‴), 69.8 (C-4″), 61.7 (C-6‴), 60.7 (C-6″); FABMS *m/z*: 643 $[M + H]^+$.

Gossypetin 7-O-β-D-glucopyranoside (3)

A yellow amorphous powder, mp 221–223°C, $[\alpha]_D^{22}$ −12.4 (*c*0.98, MeOH); IR(KBr) ν_{max} 3485, 3417, 2920, 1658, 1616, 1564, 1520, 1448, 1360, 1321, 1294, 1196, 1134, 1076, 1045, 1012, 995, 968, 899, 820, 791, 754, 640 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 11.92 (1H, s, 5-OH), 9.65 (1H, s, 3′-OH), 9.47 (1H, s, 3-OH), 9.38 (1H, s, 4′-OH), 8.59 (1H, s, 8-OH), 7.75 (1H, d, $J = 2.1$ Hz, 2′-H), 7.62 (1H, dd, $J = 8.4$ and 2.1 Hz, 6′-H), 6.89 (1H, d, $J = 8.4$ Hz, 5′-H), 6.62 (1H, s, 6-H), 4.91 (1H, d, $J = 7.5$ Hz, 1″-H), 3.72 (1H, br d, $J = 10.5$, 6″a-H), 3.48 (1H, m, 3″-H), 3.40 (1H, dd, $J = 10.5$ and 7.8 Hz, 6″b-H), 3.36 (1H, m, 2″-H), 3.20 (1H, dd, $J = 7.8$ and 7.5 Hz, 4″-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 176.2 (C-4), 151.4 (C-5), 150.2 (C-7), 147.8 (C-4″), 147.3 (C-2), 145.0 (C-3′), 143.4 (C-9), 135.6 (C-3), 126.8 (C-8), 122.1 (C-1′), 120.2 (C-6′), 115.5 (C-2′), 115.2 (C-5′), 104.6 (C-10), 101.4

(C-1″), 97.8 (C-6), 77.3 (C-3″), 75.7 (C-5″), 73.2 (C-2″), 69.7 (C-4″), 60.7 (C-6″); FABMS *m/z*: 481 $[M + H]^+$.

Herbacetin 7-O-β-D-glucopyranoside (4)

A yellow amorphous powder; ^{1}H NMR (DMSO-d_6, 500 MHz) and ^{13}C NMR (DMSO-d_6, 125 MHz) data were identical to those in literature [6]; FABMS *m/z* (%): 465 $[M + H]^+$.

Astragalin (5)

Yellow needles; ^{1}H NMR (DMSO-d_6, 500 MHz) and ^{13}C NMR (DMSO-d_6, 125 MHz) data were identical to those in literature [7]; FABMS *m/z*: 449 $[M + H]^+$.

Kaempferol 3,7-di-O-β-D-glucopyranoside (6)

A yellow amorphous powder; ^{1}H NMR (DMSO-d_6, 500 MHz) and ^{13}C NMR (DMSO-d_6, 125 MHz) data were identical to those in literature [7]; FABMS *m/z*: 611 $[M + H]^+$.

(±)-Eriodictyol 7-O-β-D-pyrannoglucuronide (7)

A white amorphous powder, $[\alpha]_D^{22}$ −43.2 (*c* 1.0, acetone–H_2O 1:1); IR(KBr) ν_{max} 3427, 1732, 1643, 1579, 1522, 1448, 1348, 1294, 1198, 1173, 1088 cm^{-1}; ^{1}H NMR (acetone-d_6, 500 MHz) and ^{13}C NMR (acetone-d_6, 125 MHz) were identical to those in literature [8]; FABMS *m/z*: 487 $[M + Na]^+$, 465 $[M + H]^+$.

(±)-Eriodictyol 7-O-β-D-pyrannoglucuronide Methyl Ester (8)

A white amorphous powder, $[\alpha]_D^{22}$ −38.6 (*c* 0.67, MeOH); ^{1}H NMR (acetone-d_6, 500 MHz) δ 12.07 (1H, s, 5-OH), 8.12 (1H, brs, 4′-OH), 8.06 (1H, brs, 3′-OH), 7.03 (1H, br s, 2′-H), 6.87 (1H, d, $J = 7.8$ Hz, 5′-H), 6.85 (1H, d, $J = 7.8$ Hz, 6′-H), 6.16 (1H, d, $J = 2.0$ Hz, 8-H), 6.12 (1H, d, $J = 2.0$ Hz, 6-H), 5.43 (1H, dd, $J = 12.6$ and 3.0 Hz, 2-H), 5.26 (1H, d, $J = 7.5$ Hz, 1″-H), 4.24 (1H, d, $J = 8.7$ Hz, 5″-H), 3.70 (1H, m, 4″-H), 3.64 (1H, m, 3″-H), 3.53 (1H, m, 2″-H), 3.23 (1H, dd, $J = 17.0$ and 12.6, H-3α), 2.75 (1H, dd, $J = 17.0$ and 3.0 Hz, H-3β), 3.68 (3H, s, OMe); ^{13}C NMR (acetone-d_6, 125 MHz) δ 197.8 (C-4), 169.5 (C-6″), 166.0 (C-7), 164.5 (C-9), 164.0 (C-5), 146.4 (C-3′), 145.9 (C-4′), 131.2 (C-1′), 119.3 (C-6′), 116.0 (C-5′), 114.7 (C-2′), 104.5 (C-10), 100.5 (C-1″), 97.4 (C-6), 96.2 (C-8), 80.0 (C-2), 76.8 (C-3″), 76.2 (C-5″), 74.0 (C-2″), 72.4 (C-4″), 52.3 (C-OMe), 43.4 (C-3); FABMS *m/z*: 479$[M + H]^+$.

(±)-Eriodictyol 7-O-β-D-pyrannoglucuronide Ethyl Ester (9)

A white amorphous powder, $[\alpha]_D^{22}$ −56.7 (*c* 0.97, MeOH); ^{1}H NMR (acetone-d_6, 500 MHz) δ 12.05 (1H, s, 5-OH), 8.07 (1H, br s, 4′-OH), 8.01 (1H, br s, 3′-OH), 7.03 (1H, br s, 2′-H), 6.87 (1H, d, $J = 7.8$ Hz, 5′-H), 6.87 (1H, d, $J = 7.8$ Hz, 6′-H), 6.16 (1H, d, $J = 2.0$ Hz, 8-H), 6.13 (1H, d, $J = 2.0$ Hz, 6-H), 5.44 (1H, dd, $J = 12.9$ and 3.3 Hz, 2-H), 5.25 (1H, d, $J = 7.5$ Hz, 1″-H), 4.20 (1H, d, $J = 8.7$ Hz, 5″-H), 3.70 (1H, m, 4″-H), 3.63 (1H, m, 3″-H), 3.53 (1H, m, 2″-H), 3.19 (1H, dd, $J = 17.0$ and 12.9, H − 3α), 2.75 (1H, dd, $J = 17.0$ and 3.3 Hz, H-3β), 4.15 (2H, q, $J = 7.0$ Hz, OCH_2CH_3), 1.23 (3H, t, $J = 7.0$ Hz, OCH_2CH_3); ^{13}C NMR (acetone-d_6, 125 MHz) δ 197.9 (C-4), 169.1 (C-6″), 166.2 (C-7), 164.6 (C-9), 164.0 (C-5), 146.5 (C-3′), 146.1 (C-4′), 131.3 (C-1′), 119.4 (C-6′), 116.1 (C-5′),

114.8 (C-2′), 104.7 (C-10), 100.8 (C-1″), 97.5 (C-6), 96.4 (C-8), 80.3 (C-2), 77.0 (C-3″), 76.6 (C-5″), 74.3 (C-2″), 72.6 (C-4″), 43.8 (C-3), 61.8 (OCH_2CH_3), 14.6 (OCH_2CH_3); FABMS *m/z*: 493 $[M + H]^+$.

Chlorogenic Acid (10)

White crystals, mp 211–213°C, $[\alpha]_D^{22}$ −98.2 (*c* 1.0, acetone–H_2O 1:1); ^{1}H NMR (acetone-d_6, 500 MHz) and ^{13}C NMR (acetone-d_6, 125 MHz) data were identical to those in literature [9,10]; FABMS *m/z*: 447 $[M + H + gly]^+$, 355 $[M + H]^+$.

Methyl Chlorogenate (11)

White crystals, mp 167–168°C, $[\alpha]_D^{22}$ −87.6 (*c* 1.2, MeOH); ^{1}H NMR (acetone-d_6, 500 MHz) and ^{13}C NMR (acetone-d_6, 125 MHz) data were identical to those in literature [11]; FABMS *m/z*: 369 $[M + H]^+$.

(−)-Eriodictyol (12)

White crystals, mp 196–197°C, $[\alpha]_D^{22}$ −12.3 (*c* 0.12, acetone); ^{1}H NMR (acetone-d_6, 500 MHz) δ 12.17 (1H, s, 5-OH), 9.57 (1H, br s, 7-OH), 8.08 (1H, brs, 3′-OH), 8.02 (1H, brs, 4′-OH), 7.02 (1H, br s, 2′-H), 6.86 (1H, d, $J = 9.0$ Hz, 5′-H), 6.85 (1H, d, $J = 9.0$ Hz, 6′-H), 5.94 (1H, d, $J = 2.0$ Hz, 8-H), 5.93 (1H, d, $J = 2.0$ Hz, 6-H), 5.39 (1H, dd, $J =$ 12.9 and 3.0 Hz, 2-H), 3.13 (1H, dd, $J = 17.0$ and 12.9, H-3α), 2.71 (1H, dd, $J =$ 17.0 and 3.0 Hz, H-3β); ^{13}C NMR (acetone-d_6, 125 MHz) data were identical to those in literature [12]; EIMS *m/z* (%): 288 $[M]^+$ (80), 271 (8), 179 (28), 166 (42), 153 (100), 136 (54), 123 (22).

Kaempferol (13)

Yellow crystals, ^{1}H NMR (acetone-d_6, 500 MHz) data were identical with those of authentic sample; EIMS *m/z* (%): 286 $[M]^+$ (100), 258 (5), 229 (7), 121 (12).

Naringenin (14)

White crystals; ^{1}H NMR (acetone-d_6, 500 MHz) data were identical with those of authentic sample; ^{13}C NMR (acetone-d_6, 125 MHz) data were identical to those in literature; EIMS *m/z* (%): 272 $[M]^+$ (85), 179 (36), 166 (35), 153 (100), 120 (78), 107 (24).

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