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# Three New Anthraquinones from *Polygonum cillinerve*

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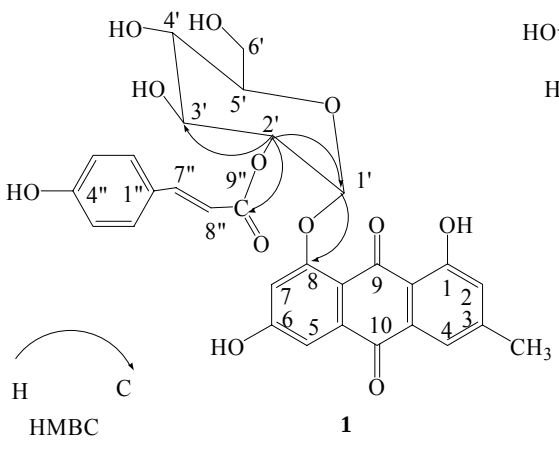
**Abstract:** Three new anthraquinones, emodin-8-β-D-(2″-*O*-coumarate)glucoside **1**, emodin-8-β-D-(6′-*O*-acetyl)glucoside **2** and physicon-8-β-D-(6′-*O*-acetyl)glucoside **3**, were isolated from the roots of *Polygonum cillinerve* and their structures were established by spectroscopic methods. The biological activity indicated that compound **1** had the scavenging activity on 1,1-diphenyl-2-picrylhydrazyl (DPPH) radicals (the $IC_{50}$ = 8.5 μmol/L), and compound **1-3** showed no activities against HL-60 and BGC-823 cells by MTT method *in vitro*.

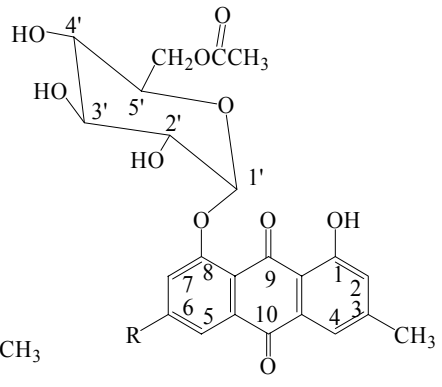
**Keywords:** *Polygonum cillinerve*, anthraquinone, antioxidant activity, cytotoxic activity.

*Polygonum cillinerve* (Nakai) Ohwi (Polygonaceae), with the Chinese name ′HongYao′, has been used in traditional Chinese medicine[1, 2] as an herbal remedy for acute stomachache and menoxenia. Recently it has been found to have obvious antioxidant activities[3]. From the roots of this plant, three new anthraquinones were isolated and named as emodin-8-β-D-(2″-*O*-coumarate)glucoside **1**, emodin-8-β-D-(6′-*O*-acetyl)-glucoside **2** and physicon-8-β-D-(6′-*O*-acetyl)glucoside **3**. Their structural elucidation was described, and spectral data were listed in **Table 1.**

**Figure 1** The structures of compound **1-3**




**1**




**2**: R=OH
**3**: R=$OCH_3$

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**Table 1** NMR data for compound **1-4** (δ ppm, *J* Hz)

| No. | | **1** | | **2** | | **3** | | **4** | |
|---|---|---|---|---|---|---|---|---|---|
| | HMBC (C→H) | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ |
| 1 | H-2 | | 161.5 | | 164.3 | | 164.8 | | 164.3 |
| 2 | H-4 | 7.01(br.s) | 123.9 | 7.18(br.s) | 119.5 | 7.20(br.s) | 119.5 | 7.00(d,*J*=1.9) | 119.4 |
| 3 | | | 146.6 | | 147.1 | | 147.3 | | 147.0 |
| 4 | H-2 | 7.36(br.s) | 131.8 | 7.49(br.s) | 124.4 | 7.51(br.s) | 124.4 | 7.29(s) | 124.3 |
| 4a | | | 118.9 | | 132.3 | | 132.2 | | 132.2 |
| 5 | H-7 | 7.28(d,*J*=2.3) | 108.5 | 7.33(d,*J*=2.4) | 108.6 | 7.41(d,*J*=2) | 107.9 | 7.16(s) | 108.6 |
| 6 | H-7 | | 164.1 | | 160.9 | | 160.4 | | 161.2 |
| 7 | H-5 | 7.06 (d,*J*=2.3) | 109.2 | 6.99(d,*J*=2.3) | 108.4 | 7.14(d,*J*=2.6) | 106.2 | 7.46(s) | 108.5 |
| 8 | H-1′,7 | | 160.4 | | 161.9 | | 161.8 | | 161.9 |
| 8a | H-5,7 | | 113.4 | | 113.6 | | 106.2 | | 113.5 |
| 9 | | | 185.8 | | 186.6 | | 186.6 | | 186.6 |
| 9a | H-2,4 | | 114.1 | | 114.6 | | 114.6 | | 114.6 |
| 10 | H-4,5 | | 182.0 | | 182.3 | | 182.0 | | 182.2 |
| 10a | | | 136.3 | | 136.7 | | 136.7 | | 136.6 |
| 1′ | H-2′ | 5.34(d,*J*=8.5) | 99.0 | 5.13(d,*J*=7.6) | 100.5 | 5.27(d,*J*=7.6) | 100.4 | 5.07(d,*J*=7.6) | 101.1 |
| 2′ | | | 77.0 | | 76.4 | | 76.4 | | 77.5 |
| 3′ | H-2′ | | 74.0 | | 73.4 | | 73.3 | | 73.4 |
| 4′ | | | 69.7 | | 70.0 | | 70.0 | | 69.7 |
| 5′ | H-2′,3′ | | 72.9 | | 74.1 | | 74.1 | | 76.6 |
| 6′ | | | 60.4 | | 63.4 | | 63.6 | | 60.8 |
| $-CH_3$ | H-2,4 | 2.33(s) | 21.2 | 2.43(s) | 21.6 | 2.44(s) | 21.5 | 2.40(s) | 21.5 |
| $-COCH_3$ | | | | 2.04(s) | 170.4, 20.7 | 2.02(s) | 170.3, 20.6 | | |
| $-OCH_3$ | | | | | | 4.00(s) | 56.3 | | |
| 1″ | H-2″,7″ | | 125.1 | | | | | | |
| 3″(5″) | H-5″ | 7.43(d,*J*=8.6) | 130.0 | | | | | | |
| 2″(6″) | H-6″ | 6.73(d,*J*=8.6) | 115.5 | | | | | | |
| 4″ | H-3″,5″,2″,6″ | | 159.5 | | | | | | |
| 8″ | | 6.31(d,*J*=15.9) | 144.1 | | | | | | |
| 7″ | H-8″ | 7.53(d,*J*=15.9) | 114.6 | | | | | | |
| 9″ | H-8″,7″,2′ | | 165.3 | | | | | | |

NMR spectra were obtained at 500 (125) MHz and recorded in DMSO-$d_6$.

Compound **1** was isolated as yellow amorphous powder, mp. 233-234℃. HREI-MS analysis revealed the molecular formula to be $C_{30}H_{27}O_{12}$ (*m/z*: 579.1485 $[M+H]^+$, calcd. 579.1503). The IR (KBr) showed absorption bands for hydroxyl (3410 $cm^{-1}$), carbonyl groups (1695, 1633$cm^{-1}$) and benzene ring (1602, 1573$cm^{-1}$) moieties. The characteristic proton signals of known compound emodin-8-β-D-glucoside **4** can be seen in the $^1H$ NMR spectrum at δ 13.12 (*br.s*,1H, 1-OH), 7.36 (*br.s*, 1H, H-4), 7.28 (*d*,1H, *J*=2.3Hz, H-5), 7.06 (*d*,1H, *J*=2.3Hz, H-7), 7.01 (*br.s*,1H, H-2), 2.33 (*s*,3H, 3-$CH_3$) and a glucose moiety at δ 5.34 (d,1H, *J*=8.5Hz) and δ 5.31~3.35(m, 6H), which is also determined by comparing its $^{13}C$ NMR spectral data with that of **4** [4]. In the $^1H$ NMR spectrum, there are signals of two olefinic protons at δ 7.53 (*d*, 1H, *J*=15.9 Hz, H-8″) and 6.31 (*d*, 1H, *J*=15.9 Hz, H-7″). By extensive analysis $^{13}C$ NMR, HMQC and EI-MS (*m/z* 431$[M-H]^-$ and 269$[M-H]^-$) spectra of compound **1**, its structure was deduced to have two groups of emodin-8-β-D-glucoside and coumaric acid units. The connectivity

of these units were established by interpreting the significant HMBC signals, which exhibited long-rang correlations between proton signal at $\delta_H$ 5.34 (H-1′) with carbon signal at $\delta_C$ 160.4 (C-8), $\delta_H$ 5.09 (H-2′) with $\delta_C$ 165.3 (C-9″), indicating glycosylation at C-8 of emodin by a coumaric acid (9″→2′) glucose moiety, which is determined by comparing its NMR spectral data with that of pieceid-2″-*O*-coumarate[3]. Compound **1** was thus determined to be emodin-8-β-D-(2″-*O*-coumarate)glucoside.

Compound **2** and **3** were isolated as yellow amorphous powder. In comparison with the NMR spectra data of emodin-8-β-D-glucoside **4**[4], the signals of **2** and **3** were in agreement with those of **4**, except for an extra signal of acetyl group [$\delta_H$ 2.02 (s, 3H); $\delta_C$ 170.4, 20.7] and methoxyl group [$\delta_H$ 4.00(s, 3H); $\delta_C$ 56.3]. These deductions were further supported by the EI-MS spectra (**2:** *m/z* 473[M-H]$^-$ and 269[M-H]$^-$; **3:** *m/z* 489 [M+H]$^+$ and 285[M+H]$^+$). Comparison of the $^{13}$C NMR spectra of **4**, the chemical shift of $\delta_C$ 60.8 (C-6′) was downfield shifted to $\delta_C$ 63.6 (C-6′) in **2, 3**. These changes indicated that the acetyl group was at C-6′in both **2** and **3**. Therefore, compounds **2** and **3** were determined as emodin-8-β-D-(6′-*O*-acetyl)glucoside and physicon-8-β-D-(6′-*O*-acetyl)glucoside, respectively.

The biological activity study indicated that compound **1** had the scavenging activity on 1,1-diphenyl-2-picrylhydrazyl (DPPH) radicals (the $IC_{50}$=8.5 μmol/L), and compound **1-3** showed no activities against HL-60 and BGC-823 cells by MTT method *in vitr*o, see **Table 2**.

**Table 2** Cytotoxic activities of compound **1-3** (n=3)**

| Sample | Concentration μg/ml | HL-60 Inhibitory% | BGC-823 Inhibitory% |
|---|---|---|---|
| **1** | 0.1 | 0.00 | 22.45 |
| | 1 | 20.30 | 15.31 |
| | 10 | 0.00 | 16.72 |
| **2** | 1 | 0.00 | 0.00 |
| | 10 | 38.93 | 2.02 |
| **3** | 1 | 0.00 | 7.29 |
| | 10 | 24.68 | 7.29 |
| * Cisplatin | 1 | 71.29 | 10.78 |
| | 10 | 94.45 | 94.87 |

*Positive control
**Conducted by the national laboratory of New Drug Screen of China Pharmaceutical University

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