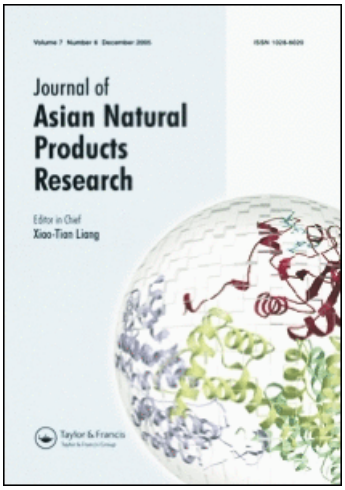

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Two new flavonoid glycosides from the whole herbs of *Hyssopus officinalis*

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Two new flavonoid glycosides from the whole herbs of *Hyssopus officinalis*

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Two new flavonoid glycosides, quercetin 7-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside (**1**) and quercetin 7-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside 3′-*O*-β-D-glucopyranoside (**2**), together with nine known flavonoids were isolated from the whole herbs of *Hyssopus officinalis* L. cultivated in Xinjiang Uygur Autonomous Region of China. All structures were characterized by the spectroscopic methods including UV, IR, ESI-MS, 1D, and 2D NMR. Their potent free radical scavenging activity against the stable 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical was evaluated.

Keywords: *Hyssopus officinalis* L.; flavonoid; quercetin 7-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside; quercetin 7-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside 3′-*O*-β-D-glucopyranoside; free radical scavenging activity; DPPH

1. Introduction

Hyssopus belongs to the Lamiaceae family, and some species are used as traditional folk medicines for the treatment of asthma, cough, bronchitis, fever, trauma, and rheumatism by Uighur in Xinjiang Uygur Autonomous Region of China. *Hyssopus officinalis* L. grows in Europe and is cultivated in Xinjiang, China. Previous studies have revealed that the essential oil of *H. officinalis* possessed antibacterial, spasmolysant, muscle relaxing, antifungal, and antiplatelet activities [1–4]. On the bioactivity of the extract of *H. officinalis*, α-glucosidase inhibitory activity was found in aqueous methanol extract [5], the *n*-hexane extract exhibited a strong inhibitory potency against angiotensin-converting enzyme [6], and the aqueous extract showed the antiaging effect [7]. *H. officinalis* was also quite effective in treating asthma by inhibiting the production of IL-4, regulating the balance of Th1 and Th2 cytokines, and restraining the assemble of inflammatory cell to treat allergic asthma [8]. It was reported that the active antioxidant components can be isolated from the alcoholic extract of *H. officinalis* [9]. Our chemical studies on the whole herbs resulted in the isolation and purification of two new flavonoids, quercetin 7-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside (**1**) and quercetin 7-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside 3′-*O*-β-D-glucopyranoside (**2**), together with nine known ones apigenin (**3**), apigenin 7-*O*-β-D-glucopyranoside (**4**), apigenin 7-*O*-β-D-glucuronopyranoside methyl ester (**5**), luteolin (**6**), apigenin 7-*O*-β-D-glucuronide (**7**), apigenin 7-*O*-β-D-glucuronopyranoside butyl ester (**8**), luteolin 7-*O*-β-D-glucopyranosid (**9**), diosmin (**10**), and acacetin 7-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside

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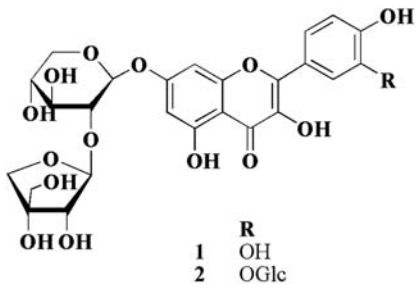
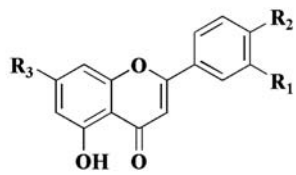


	R
1	OH
2	OGlc



	R_1	R_2	R_3
3	H	OH	OH
4	H	OH	OGlc
5	H	OH	OGluA methyl ester
6	OH	OH	OH
7	H	OH	OGluA
8	H	OH	OGluA butyl ester
9	OH	OH	OGlc
10	OH	OMe	ORha-(1→6)-Glc
11	H	OMe	ORha-(1→6)-Glc

Figure 1. Structures of compounds **1**–**11**.

(**11**). Herein, we report the isolation and structural elucidation of two new flavonoid compounds on the basis of spectroscopic methods including MS, IR, UV, 1D, and 2D NMR. The compounds **4**–**9**, and **11** were isolated from the genus *Hyssopus* for the first time. At the same time, the potent free radical scavenging activity of the compounds **1**–**11** against the stable 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical was evaluated.

2. Results and discussion

Compound **1** (Figure 1) was obtained as a yellow powder. Its molecular formula was determined as $C_{25}H_{26}O_{15}$ on the basis of HR-ESI-MS data at *m/z* 567.1345 $[M + H]^+$ and 589.1164 $[M + Na]^+$. Its IR spectrum indicated the presence of hydroxyl groups (3384 cm^{-1}), a carbonyl carbon (1655 cm^{-1}), and the benzene ring (1597 and 1498 cm^{-1}). The ^1H NMR spectrum of **1** gave phenol proton signals at δ_H 12.50 (1H, s) and δ_H 9.64 (1H, s), which were characteristic signals of 5-OH and 3-OH, respectively. The signals at δ_H 6.35 (1H, d, $J = 2.0$ Hz) and 6.72 (1H, d, $J = 2.0$ Hz) indicated the H-6 and H-8 of A-ring. In the HMBC spectrum (Figure 2) of **1**, the signal at δ_H 6.35 (H-6) correlated with δ_C 160.4 (C-5), 162.2 (C-7), 94.0 (C-8), 104.7 (C-10) and the signal at δ_H 6.72 (H-8) showed correlations with the carbons at δ_C 98.5 (C-6), 162.2 (C-7), 155.7 (C-9), 104.7 (C-10). A typical ABX spin coupling system was showed by the signals at δ_H 7.71 (1H, d, $J = 2.0$ Hz), 6.89 (1H, d, $J = 8.4$ Hz), and 7.57 (1H, dd, $J = 8.4$, 2.0 Hz), suggesting the presence of 3′,4′-disubstituted B-ring. Thus, the aglycone was elucidated as quercetin. The signals of anomeric protons at δ_H 5.32 (1H, d, $J = 1.6$ Hz) and 5.17 (1H, d, $J = 7.2$ Hz) were the characteristics of apiose and xylose, respectively, in the ^1H NMR spectrum. In addition, in the HMQC spectrum of **1**, the protons at δ_H 5.32 (1H, d, $J = 1.6$ Hz) and 5.17 (1H, d, $J = 7.2$ Hz) were correlated with carbon

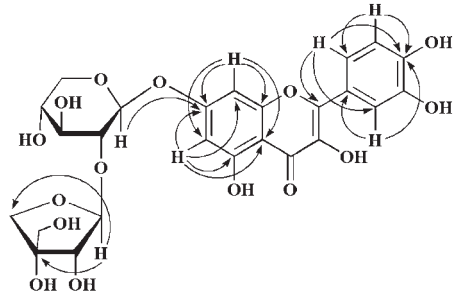


Figure 2. Key HMBC correlations of **1**.

signals at δ_C 108.8 and 98.5, respectively. The glycosyl moieties of **1** were established by comparing the data of the ^{13}C NMR, HMQC, and HMBC spectra with previous reports in the literature [10]. The xylosyl anomeric proton at δ_H 5.17 (xylosyl H-1) was correlated with C-7 at δ_C 162.2, and the apiosyl anomeric proton at δ_H 5.32 (apiosyl H-1) had correlation with the carbon at δ_C 76.6 (xylosyl C-2) in the HMBC experiment, implying that the apiosyl group was linked with the 2-OH of the xylosyl group. On the basis of all the data above, the structure of **1** was determined to be quercetin 7-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside.

Compound **2** (Figure 1) was also obtained as a yellow powder, whose molecular formula was established as $C_{31}H_{36}O_{20}$ by HR-ESI-MS data at *m/z* 729.1873 $[M + H]^+$ and 751.1692 $[M + Na]^+$. Its molecular ion was 162 mass units bigger than that of **1**, which corresponded to the difference in the number of glucosyl group. The aglycone of **2** also was quercetin. That compound was deduced from the following information in the ^1H NMR spectrum: the signals at δ_H 12.46 (1H, s, 5-OH), 9.60 (1H, s, 3-OH), 6.34 (1H, d, $J = 2.0$ Hz, H-6), 6.84 (1H, d, $J = 2.0$ Hz, H-8), 8.02 (1H, d, $J = 2.0$ Hz, H-2′), 6.98 (1H, d, $J = 8.4$ Hz, H-5′), and 7.90 (1H, dd, $J = 8.4$, 2.0 Hz, H-6′); in the HMQC spectrum: the proton at δ_H 6.34 (1H, d, $J = 2.0$ Hz, H-6) was correlated with the carbon at δ_C 98.4 (C-6) and the proton at δ_H 6.84 (1H, d, $J = 2.0$ Hz, H-8) was correlated with the carbon at δ_C 94.1 (C-8); and in the HMBC spectrum (Figure 3): the signal at δ_H 6.34 (1H, d, $J = 2.0$ Hz, H-6) was correlated with C-5 at δ_C 160.3, C-7 at δ_C 162.2, C-8 at δ_C 94.1, and C-10 at δ_C 104.8, and the signal at δ_H 6.84 (1H, d, $J = 2.0$ Hz, H-8) was correlated with C-6 at δ_C 98.4, C-7 at δ_C 162.2, C-9 at δ_C 155.8, and C-10 at δ_C 104.8. Comparing the spectroscopic data of **2** with **1** and that stated in the literature [10], an additional β-D-glucopyranosyl structure was identified. The HMQC spectrum exhibited the correlation of the proton at δ_H 4.76 (glucosyl H-1) with the carbon at δ_C 102.6 (glucosyl C-1). Meanwhile, in the HMBC analysis, the signals at δ_H 4.76 (1H, d, $J = 7.2$ Hz, glucosyl H-1) correlated with C-3′ at δ_C 145.4, which also showed correlations with H-2′ at δ_H 8.02, H-5′ at δ_H 6.98 in the HMBC experiment. Therefore, the structure of **2** was elucidated as quercetin 7-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside-3′-*O*-β-D-glucopyranoside.

Compounds **3**–**11** were identified as apigenin [11], apigenin 7-*O*-β-D-glucopyranoside [12], apigenin 7-*O*-β-D-glucuronopyranoside methyl ester [13], luteolin [14], apigenin 7-*O*-β-D-glucuronide [12], apigenin 7-*O*-β-D-glucuronopyranoside butyl ester [13], luteolin 7-*O*-β-D-glucopyranoside [15], diosmin [16], and acacetin 7-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside [17].

The extract of *H. officinalis* possessed antioxidant activity [18]. Thus, the free radical scavenging activity of compounds **1**–**11** (chemical structures shown in Figure 1) was evaluated using DPPH with butylated hydroxytoluene (BHT) and ascorbic acid, used as reference compounds [19]. The results were summarized in Table 1. Of these compounds, **1**, **2**, **6**, and **9** with IC_{50} values in the range of 2.81–10.41 μmol/L exhibited stronger scavenging activity on DPPH assay than BHT ($IC_{50} = 75.38$ μmol/L) and L-ascorbic

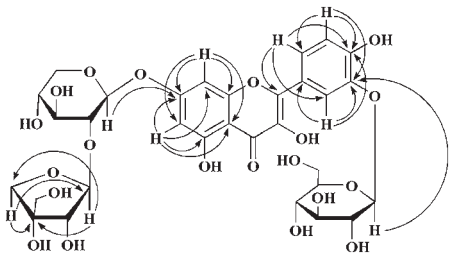


Figure 3. Key HMBC correlations of **2**.

Table 1. DPPH scavenging activity of isolated compounds.

Compound	IC_{50} (μmol/L)
1	2.81
2	10.41
3	>1000
4	>1000
5	>1000
6	3.08
7	>1000
8	696.73
9	3.54
10	360.69
11	>1000
BHT	75.38
L-ascorbic acid	16.47

acid (IC_{50} = 16.47 μmol/L). The DPPH scavenging activity of **1** was better than **2** that possessed monohydroxyl substitution in the B-ring. Compounds **3**–**5**, **7**, and **11** without 3′-OH possessed less activity on DPPH. These trends were consistent with the report that substitution patterns on the B-ring affected antioxidant potencies of the flavonoids, and the di-OH substitution at C-3′ and C-4′ was particularly important to the oxygen radical absorbing activity of a flavonoid [20,21].

3. Experimental

3.1 General experimental procedures

Optical rotation was determined on an Autopol III polarimeter (Rudolph Research Analytical, Flanders, NJ, USA) with MeOH as solvent. IR data were measured on a Nicolet NEXUES-470 FT-IR instrument. UV spectra were acquired on a Cary 300 spectrophotometer. FT-ESI-MS and HR-ESI-MS spectra were recorded on a Bruker APEX IV FT-MS (7.0T) mass spectrometer. 1D and 2D NMR spectra were taken on a Bruker AV 400 spectrometer with TMS as internal standard. TLC and column chromatography (CC) were performed on silica gel plates and silica gel G separately (TLC: GF_{254} and CC: 200–300 mesh, Qingdao Marine Chemical Co., Ltd., Qingdao, China), Sephadex LH-20 (GE Healthcare, Uppsala, Sweden), polyamide (Taizhou Si-Jia Biochemical Plastic Company, Taizhou, China), and macroporous resins AB-8 (Resin Factory of Nankai University, Tianjin, China). DPPH and L-ascorbic acid were purchased from Sigma-Aldrich Co. (St Louis, MO, USA). BHT was purchased from DIMA Technology, Inc. (San Dimas, CA, USA). UV_{max} Kinetic Microplate Reader (Molecular Dynamics, Inc., Sunnyvale, CA, USA) was used as a microplate reader. 96-well plates were purchased from Corning Costar (Cambridge, MA, USA).

3.2 Plant material

The whole herbs of *H. officinalis* were collected at Xinjiang Uygur Autonomous Region of China, in 2005, and identified by Prof. Xiu-Wei Yang, State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, China. A voucher specimen (No. 2006081) has been deposited in the Department of Natural Medicines, School of Pharmaceutical Sciences, Peking University.

3.3 Extraction and isolation

The dried whole herbs of *H. officinalis* (6.3 kg) were extracted with 95% EtOH under reflux at room temperature. The ethanolic extract was concentrated *in vacuo* and suspended in water, and then successively partitioned with petroleum ether, EtOAc, and *n*-BuOH. The EtOAc extract (60 g) was chromatographed on silica gel using a system of $CHCl_3$–MeOH (100:0 → 0:100) to afford five fractions. Fraction 5 (7.8 g) was rechromatographed over silica gel eluting with $CHCl_3$–MeOH (17:1 → 1:1) to yield three fractions (5-1, 5-2, and 5-3). Fraction 5-2 was further purified by repeated CC on silica gel eluting with $CHCl_3$–MeOH (8:1, 4:1) and

Table 2. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) data of **1** and **2** in DMSO-d_6.

	1		**2**	
Position	δ_H	δ_C	δ_H	δ_C
2	–	147.6	–	147.0
3	–	136.1	–	136.4
4	–	176.0	–	176.1
5	–	160.4	–	160.3
6	6.35 (1H, d, $J = 2.0$ Hz)	98.5	6.34 (1H, d, $J = 2.0$ Hz)	98.4
7	–	162.2	–	162.2
8	6.72 (1H, d, $J = 2.0$ Hz)	94.0	6.84 (1H, d, $J = 2.0$ Hz)	94.1
9	–	155.7	–	155.8
10	–	104.7	–	104.8
1′	–	120.1	–	122.1
2′	7.71 (1H, d, $J = 2.0$ Hz)	115.3	8.02 (1H, d, $J = 2.0$ Hz)	116.0
3′	–	145.0	–	145.4
4′	–	147.9	–	149.0
5′	6.89 (1H, d, $J = 8.4$ Hz)	115.6	6.98 (1H, d, $J = 8.4$ Hz)	116.0
6′	7.57 (1H, dd, $J = 8.4$, 2.0 Hz)	121.8	7.90 (1H, dd, $J = 8.4$, 2.0 Hz)	123.9
3-OH	9.64 (1H, s)		9.60 (1H, s)	
5-OH	12.50 (1H, s)		12.46 (1H, s)	
Xyl				
1	5.17 (1H, d, $J = 7.2$ Hz)	98.5	5.14 (1H, d, $J = 7.5$ Hz)	98.6
2	3.73 (1H, dd, $J = 7.2$, 12.0 Hz)	76.6	3.74 (1H, dd, $J = 7.6$, 11.2 Hz)	76.7
3	3.50 (1H, dd, $J = 8.1$, 12.0 Hz)	75.7	3.48 (1H, dd, $J = 8.0$, 11.2 Hz)	75.7
4	3.35 (1H, m)	69.4	3.38 (1H, m)	69.4
5	3.40 (1H, dd, $J = 8.0$, 11.2 Hz)	65.6	3.39 (1H, dd, $J = 8.0$, 12.0 Hz)	65.7
	3.77 (1H, dd, $J = 3.6$, 11.2 Hz)		3.81 (1H, dd, $J = 4.8$, 12.0 Hz)	
Api				
1	5.32 (1H, d, $J = 1.6$ Hz)	108.8	5.33 (1H, d, $J = 1.2$ Hz)	108.8
2	3.74 (1H, d, $J = 1.6$ Hz)	76.1	3.77 (1H, d, $J = 1.2$ Hz)	76.1
3	–	79.2	–	79.3
4	3.64 (1H, d, $J = 9.2$ Hz)	73.9	3.64 (1H, d, $J = 9.4$ Hz)	74.0
	3.88 (1H, d, $J = 9.2$ Hz)		3.88 (1H, d, $J = 9.4$ Hz)	
5	3.27 (1H, d, $J = 11.5$ Hz)	64.1	3.30 (1H, d, $J = 12.0$ Hz)	64.1
	3.28 (1H, d, $J = 11.5$ Hz)		3.31 (1H, d, $J = 12.0$ Hz)	
Glc				
1			4.76 (1H, d, $J = 7.2$ Hz)	102.6
2			3.32 (1H, dd, $J = 7.2$, 8.5 Hz)	73.3
3			3.30 (1H, m)	75.9
4			3.21 (1H, m)	69.9
5			3.38 (1H, dd, $J = 7.6$, 8.5 Hz)	77.3
6			3.49 (1H, dd, $J = 7.6$, 11.5 Hz)	60.8
			3.53 (1H, dd, $J = 4.0$, 11.5 Hz)	

Sephadex LH-20 (MeOH–H_2O 80:20) to give compounds **3** (27 mg) and **6** (10 mg). Fraction 5-3 was purified by polyamide ($CHCl_3$–MeOH, 4:1 and 1:1) and Sephadex LH-20 (MeOH) column to furnish **4** (15 mg) and **5** (8 mg). The *n*-BuOH extract (62 g) was applied to macroporous resin AB-8 and eluted with a gradient of EtOH–H_2O (0:100 → 100:0) to yield four fractions (1–4). Compound **8** (11 mg) was obtained by precipitation from fraction 2 (17.1 g) with MeOH. Fraction 3 (14.5 g) was separated on silica gel CC eluted with EtOAc–MeOH–H_2O (50:2:1 → 5:2:1) and fractions A–F were collected. Fraction A (2.8 g) was purified by polyamide CC using $CHCl_3$–MeOH (15:1) and Sephadex LH-20 using MeOH–H_2O

(4:1) to get compounds **7** (9 mg) and **9** (33 mg). Fraction D (1.3 g) was applied to the polyamide CC eluted with EtOH–H_2O (1:2) and purified over Sephadex LH-20 column using MeOH–H_2O (80:20) to get compound **10** (22 mg). Fraction E (2.4 g) was subjected to the polyamide CC eluted with EtOAc–MeOH (8:1–1:1) and further purified over Sephadex LH-20 column using the elution MeOH–H_2O (4:1), then compounds **1** (5 mg), **2** (7 mg), and **11** (12 mg) were received.

*3.3.1 Quercetin 7-O-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside (**1**)*

Yellow amorphous powder; $[\alpha]_D^{23}$ −8.37 ($c = 0.15$, MeOH); UV λ_{MeOH} nm (log ε): 256 (3.98), 373 (3.86); IR (KBr) ν_{max} (cm^{-1}): 3384, 1655, 1597, 1498, 1040; ESI-MS *m/z* 567 $[M + H]^+$; ^1H and ^{13}C NMR spectral data, see Table 2; HR-ESI-MS *m/z* 567.1345 $[M + H]^+$ (calcd for $C_{25}H_{27}O_{15}$, 567.1350), 589.1164 $[M + Na]^+$ (calcd for $C_{25}H_{26}O_{15}Na$, 589.1169).

*3.3.2 Quercetin 7-O-β-D-apiofuranosyl-(1 → 2)-β-D-xylopyranoside-3′-O-β-D-glucopyranoside (**2**)*

Yellow amorphous powder; $[\alpha]_D^{23}$ −66.09 ($c = 0.09$, MeOH); UV λ_{MeOH} nm (log ε): 253 (4.09), 364 (4.03); IR (KBr) ν_{max} (cm^{-1}): 3384, 1655, 1597, 1498, 1040. ^1H and ^{13}C NMR spectral data, see Table 2; ESI-MS *m/z* 729.13 $[M + H]^+$, 750.97 $[M + Na]^+$, 766.78 $[M + K]^+$; HR-ESI-MS *m/z* 729.1873 $[M + H]^+$ (calcd for $C_{31}H_{37}O_{20}$, 729.1878), 751.1692 $[M + Na]^+$ (calcd for $C_{31}H_{36}O_{20}Na$, 751.1698).

3.4 DPPH free radical scavenging activity

The free radical scavenging activity of compounds **1**–**11** was determined using DPPH as a reagent with BHT and ascorbic acid used as standards with some modifications [19,22]. Each MeOH solution (150 μl) of compounds **1**–**11** at various concentrations (0.1–1000 μmol/L) was mixed with a 200-μmol/L solution (50 μl) of DPPH/MeOH in a 96-well microtiter plate. The reaction mixtures were incubated for 30 min in a dark room at room temperature. The absorbance was read by a microplate reader at 490 nm. Finally, the percentage of DPPH scavenging effect was calculated with the following equation:

$$\text{DPPH scavening effect (\%)} = [(A_0 - A_1)/A_0] \times 100\%,$$

where A_1 is the absorbance of the samples and the standards, and A_0 is the absorbance of the control.

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