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PHENYLPROPANOID GLYCOSIDES FROM *Conyza japonica*

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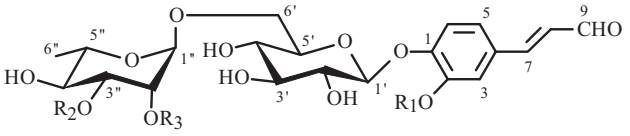
*Three new phenylpropanoid glycosides, named 1-*O*-[3-*O*-acetyl-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-3-hydroxycinnamaldehyde (**1**), 1-*O*-[2,3-*O*-diacetyl-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-3-methoxycinnamaldehyde (**2**), and 1-*O*-[3-*O*-acetyl-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-4-allyl-2-methoxyphenol (**3**), were isolated from the 95% EtOH extract of the dry fronds of* Conyza japonica. *The structures of the new compounds were elucidated by spectral methods.*

Keywords: *Conyza japonica*, phenylpropanoid glycosides, Compositae.

The genus *Conyza* comprises about 50 species, which grow mainly in tropical and subtropical areas [1]. *Conyza japonica* (Thunb.) Less. is a perennial herbaceous plant distributed mainly in the southern regions of the People′s Republic of China at altitude 700–2500 m above sea level [2, 3]. In folk medicine, its aerial parts are used to treat some kinds of inflammatory disease, especially chronic bronchitis [4–8]. The present study was undertaken to investigate the chemical constituents of the 95% EtOH extract of the dry fronds of *C. japonica* from Yuanjiang, Yunnan Province, which led to the isolation of three new phenylpropanoid glycosides, named 1-*O*-[3-*O*-acetyl-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyl]-3-hydroxycinnamaldehyde (**1**), 1-*O*-[2,3-*O*-diacetyl-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyl]-3-methoxycinnamaldehyde (**2**), and 1-*O*-[3-*O*-acetyl-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyl]-4-allyl-2-methoxyphenol (**3**). This paper deals with the structural elucidation on the basis of spectroscopic analysis, including 1D NMR, 2D NMR, and HR-ESI-MS.



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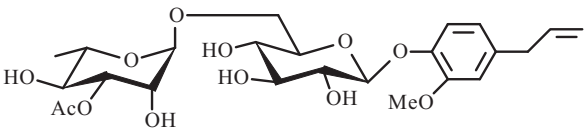

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1: $R_1 = R_3 = H$, $R_2 = Ac$
2: $R_1 = Me$, $R_2 = R_3 = Ac$

Compound **1** was obtained as a white amorphous solid, and its molecular formula was indicated as $C_{23}H_{30}O_{13}$ by HR-ESI-MS ($[M - H]^-$ at *m*/*z* 513.1605; calcd 513.1608), corresponding to nine unsaturation degrees. Strong broad absorption at 3450 cm^{-1} and 1685 cm^{-1} in the IR spectrum of **1** indicated the presence of OH and CHO, respectively. The ^{13}C NMR and DEPT spectra of **1** showed resonances characteristic of a phenylpropanoid, two hexoses, and one Ac group (Table 1). The ^1H NMR spectrum displayed signals for a 1,2,4-trisubstituted aromatic ring [δ 6.72 (1H, d, J = 1.8 Hz), 6.62 (1H, dd, J = 8.2, 1.8 Hz), and 6.46 (1H, d, J = 8.2 Hz)], two olefinic protons at 5.90 (d, J = 16.8 Hz) and 7.21 (dd, J = 16.8, 7.8 Hz) for a disubstituted trans double bond, and an aldehyde group [9.68 (1H, d, J = 7.8 Hz)]. Acid hydrolysis of **1** with 1 M HCl in dioxane–H_2O (1:1) gave cinnamaldehyde ($C_9H_8O_3$), D-glucose, and L-rhamnose as the carbohydrate components. The monosaccharides, including their absolute configurations, were identified by direct HPLC analysis of the hydrolysate, with detection being carried out using an optical rotation (OR) detector.

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TABLE 1. ^{1}H NMR and ^{13}C NMR Data of Compounds **1–3** (CD_3OD, δ, ppm, J/Hz)

C atom	**1**		**2**		**3**	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	146.7 (s)	–	146.5 (s)	–	146.2 (s)	–
2	149.4 (s)	–	151.3 (s)	–	151.0 (s)	–
3	115.1 (d)	6.72 (d, J = 1.8)	114.8 (d)	6.78 (d, J = 1.8)	114.3 (d)	6.83 (d, J = 1.8)
4	127.8 (s)	–	128.0 (s)	–	136.6 (s)	–
5	123.0 (d)	6.62 (dd, J = 8.2, 1.8)	122.8 (d)	6.61 (dd, J = 8.2, 1.8)	122.1 (d)	6.73 (dd, J = 8.2, 1.8)
6	116.5 (d)	6.46 (d, J = 8.2)	116.8 (d)	6.51 (dd, J = 8.2, 1.8)	118.6 (d)	7.04 (dd, J = 8.2, 1.8)
7	151.9 (d)	5.90 (d, J = 16.8)	152.1 (d)	5.92 (d, J = 16.8)	40.8 (t)	3.30 (d, J = 6.8)
8	129.0 (d)	7.21 (dd, J = 16.8, 7.8)	129.0 (d)	7.22 (dd, J = 16.8, 7.8)	139.0 (d)	5.94 (m)
9	191.2 (d)	9.68 (d, J = 7.8)	190.0 (d)	9.70 (d, J = 7.8)	115.9 (t)	5.05 (dd, J = 16.8, 2.3)
O-Glc						
1′	104.8 (d)	4.78 (d, J = 8.0)	103.1 (d)	4.82 (d, J = 8.0)	103.9 (d)	4.80 (d, J = 8.0)
2′	74.8 (d)	3.18 (m)	74.3 (d)	3.17 (m)	75.0 (d)	3.20 (m)
3′	77.3 (d)	3.34 (m)	76.8 (d)	3.36 (m)	77.1 (d)	3.39 (m)
4′	71.8 (d)	3.27 (m)	71.4 (d)	3.26 (m)	71.7 (d)	3.31 (m)
5′	77.9 (d)	3.68 (m)	77.7 (d)	3.73 (m)	77.8 (d)	3.71 (m)
6′	66.7 (t)	3.98 (dd, J = 13.0, 6.6)	67.8 (t)	4.02 (dd, J = 13.0, 6.6)	68.2 (t)	4.00 (dd, J = 13.0, 6.6)
		3.63 (dd, J = 13.0, 6.6)		3.69 (dd, J = 13.0, 6.6)		3.68 (dd, J = 13.0, 6.6)
O-Rha						
1″	102.9 (d)	4.74 (d, J = 1.3)	103.6 (d)	4.78 (d, J = 1.3)	102.0 (d)	4.72 (d, J = 1.3)
2″	70.0 (d)	4.13 (m)	70.2 (d)	4.10 (m)	69.8 (d)	4.12 (m)
3″	70.6 (d)	4.10 (m)	69.0 (d)	4.42 (m)	70.2 (d)	4.08 (m)
4″	74.2 (d)	3.86(m)	72.6 (d)	4.21 (m)	73.6 (d)	3.82 (m)
5″	67.9 (d)	3.82 (m)	65.6 (d)	3.80 (m)	67.6 (d)	3.78 (m)
6″	17.8 (q)	1.24 (d, J = 6.0)	17.8 (q)	1.20 (d, J = 6.0)	17.8 (q)	1.21 (d, J = 6.0)
OMe	–	–	56.8 (q)	3.82 (s)	56.8 (q)	3.84 (s)
C=O	172.8 (s)	–	173.0 (s)	–	172.5 (s)	–
Me	21.2 (q)	2.09 (s)	21.3 (q)	2.07 (s)	21.1 (q)	2.07 (s)
C=O	–	–	171.9 (s)	–	–	–
Me	–	–	20.7 (q)	2.01 (s)	–	–

The rhamnopyranosyl and glucopyranosyl units were in the *α*- and *β*-configurations, respectively, by the coupling constants of their anomeric protons (Table 1). In the HMBC plot, the correlation between the anomeric proton (δ 4.74) of the rhamnosyl unit and C-6′ (δ 66.7) of the glucopyranosyl unit identified a rhamnosyl (1→6) glucopyranosyl linkage. The C-2″ location of the acetyl group in the rhamnosyl unit was confirmed by HMBC correlation of H-2″ (δ 4.13) with the carbonyl carbons (δ 172.8) of the acetyl group. Furthermore, the sugar chain was linked to C-1 of the aglycone by HMBC correlation of the anomeric proton (δ 4.78) of the glucopyranosyl unit and C-1 (δ 146.7) of the aglycone. Accordingly, the structure of **1** was established as 1-*O*-[3-*O*-acetyl-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyl]-3-hydroxycinnamaldehyde.

Compound **2**, a white amorphous powder, was established as $C_{26}H_{34}O_{14}$ according to its HR-ESI-MS (*m/z* 569.1867 $[M - H]^-$; calcd 569.1870). Comparison of the NMR data of **2** with those of **1** revealed that the only significant difference is that there is one more acetyl group and one more methoxy group in **2**. The HMBC correlations of H-2″ (δ 4.10) and H-3″ (δ 4.42) with the two carbonyl carbons (δ 171.9 and 173.0) of the acetyl groups, respectively, indicated the C-2″ and C-3″ locations of the acetyl groups in the rhamnosyl unit. The HMBC correlations between OMe with C-2 suggested that OMe was linked at C-2 of the aglycone. All of these data for **2** were consistent with the structure of 1-*O*-[2,3-*O*-diacetyl-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyl]-3-methoxycinnamaldehyde.

Compound **3**, a white amorphous powder, was assigned the molecular formula $C_{24}H_{34}O_{12}$ on the basis of its HR-ESI-MS (*m/z* 513.1978 ($[M - H]^-$, calcd 513.1972). The ^{1}H and ^{13}C NMR data of the aglycone of **3** were closely similar to those of **2**, except that the signals of the fragment –CH=CH–CHO in **2** were replaced by the signals of the $–CH_2–CH=CH_2$ in **3**. The HMBC correlations of H-2″ (δ_H 4.12) with the carbonyl carbons (δ 172.5) of the acetyl group indicated the C-2″ locations of the acetyl group in the rhamnosyl unit. Thus, the structure of **3** was determined as 1-*O*-[3-*O*-acetyl-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyl]-4-allyl-2-methoxyphenol.

EXPERIMENTAL

General Procedures. Column chromatography (CC): silica gel (200–300 mesh, 10–40 μm; Qingdao Marine Chemical Factory, Qingdao, P. R. China), C_{18} reverse-phase silica gel (60 mm; Merck), Sephadex LH-20 (Amersham Pharmacia Biotech, Sweden). Thin-layer chromatography (TLC): silica gel GF_{254} (10–40 μm; Qingdao Marine Chemical Factory, Qingdao, P. R. China). MCI Gel CHP20P (75–150 μm; Mitsubishi Kasei Chemical Industries), C_{18} reversed-phase silica gel (20–45 um; Fuji Silysia Chemical Ltd.). All solvents were distilled before use. HPLC (anal. and prep.): Shimadzu model LC-8A on YMC-pack, R & D ODS column (250 × 4.6 mm, 250 × 20 mm) and UV detector Shimadzu SPD-10AVP. Melting points: Tempo melting-point apparatus, uncorrected. Optical rotations: JASCO-20C digital polarimeter. UV spectra: Hewlett-Packard-8452A diode-array spectrophotometer. IR spectra: Perkin–Elmer 577 spectrometer, in cm^{-1}. ^1H and ^{13}C NMR spectra: Bruker AM-400 spectrometer, δ in ppm, J in Hz. MS: VG AutoSpec-3000 mass spectrometer, in *m/z*. HR-ESI-MS: API QSTAR Pulsar-1 mass spectrometer.

Plant Material and Extraction and Isolation. The fronds of *C. japonica* were collected in Yuanjiang, Yunnan Province, P. R. China, in July 2010. A specimen (CJ20100701), identified by one of the authors (J. G. Chen), was deposited in the Herbarium of the College of Biological Resources and Environment Science, Qujing Normal University, Qujing, P. R. China. The dry fronds of *C. japonica* (1.0 kg) were extracted with 95% EtOH (3 × 5 L) for 24 h at r.t. After removal of EtOH under reduced pressure, the aqueous brownish syrup (1 L) was suspended in H_2O (500 mL) and then partitioned with AcOEt to afford an AcOEt extract (35 g). The AcOEt-soluble extract was subjected to chromatography over SiO_2 column, eluting with gradient $CHCl_3$–MeOH to afford six fractions, Frs.1-6. Fractions 3 (61 g) and 4 (6.3 g) were repeatedly purified by SiO_2 column chromatography (Sephadex LH-20, RP-18) and semi-preparative HPLC to yield **1** (6.8 mg), **2** (7.1 mg), and **3** (7.9 mg).

1-*O*-[3-*O*-Acetyl-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-3-hydroxycinnamaldehyde (1). White amorphous powder; $[\alpha]_D^{20}$ –159.03° (*c* 0.003, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 205 (2.78). IR (KBr, ν_{max}, cm^{-1}): 3450, 2940, 2870, 1685, 1460, 1390, 1027. ^1H and ^{13}C NMR data are shown in Table 1. FAB-MS (neg.): 513 $[M - H]^-$; HR-ESI-MS: *m/z* 513.1605 $[M - H]^-$; calcd 513.1608.

1-*O*-[2,3-*O*-Diacetyl-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-3-methoxycinnamaldehyde (2). White amorphous powder; $[\alpha]_D^{20}$ –200.01° (*c* 0.025, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 205 (2.15). IR (KBr, ν_{max}, cm^{-1}): 3450, 2938, 2876, 1685, 1455, 1380, 1020. ^1H and ^{13}C NMR data are shown in Table 1; FAB-MS (neg.): 569 $[M - H]^-$; HR-ESI-MS: *m/z* 569.1867 $[M - H]^-$; calcd 569.1870.

1-*O*-[3-*O*-Acetyl-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl]-4-allyl-2-methoxyphenol (3). White amorphous powder; $[\alpha]_D^{20}$ –213.03° (*c* 0.004, MeOH). UV (MeOH, λ_{max}, nm) (log ε): 204 (3.15). IR (KBr, ν_{max}, cm^{-1}): 3350, 2942, 2873, 1700, 1664, 1461, 1389, 1094, 1027. ^1H and ^{13}C NMR data are shown in Table 1. FAB-MS (neg.): 513 $[M - H]^-$; HR-ESI-MS: *m/z* 513.1978 $[M - H]^-$; calcd 513.1972.

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