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Iridoid glycosides and cucurbitacin glycoside from *Neopicrorhiza scrophulariiflora*

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Abstract

Three iridoid glycosides, picrorosides A (**1**), B (**2**) and C (**3**), and a cucurbitacin glycoside, scrophoside A (**4**), were isolated from the rhizomes of *Neopicrorhiza scrophulariiflora* (Scrophulariaceae), along with two known iridoid glycosides, picrosides I (**5**) and II (**6**), and three known cucurbitacin glycosides (**7**–**9**). Their structures were elucidated on the basis of both chemical and spectroscopic data.

Keywords: *Neopicrorhiza scrophulariiflora*; Scrophulariaceae; Iridoid glycoside; Cucurbitacin glycoside; Picrorosides A, B and C; Scrophoside A

1. Introduction

Neopicrorhiza scrophulariiflora (Pennell) Hong, a raw material exclusively used as pharmaceuticals in Japan, is distributed throughout the high altitude (>4400 m) regions in southeastern Tibet and the northwestern Yunnan Province of China (Wang et al., 1993). Iridoid glycosides (Li et al., 2000), triterpenoids (Smit et al., 2000), phenolic glycosides (Wang et al., 2004), and phenylethanoid glycosides (Li et al., 1998) have all been isolated from the rhizomes of this plant. Recently, the Ministry of Health, Labour and Welfare of Japan began to study the reclassification of raw materials exclusively used as pharmaceuticals, and a number of herbs were investigated for their toxicity and secondary metabolites. In our previous paper (Kim et al., 2006), we reported the isolation and structural elucidation of two phenylpropanoid glycosides, scrophulosides A and B. In further studies on the rhizomes of this plant, we isolated three new iridoid glycosides, picrorosides A (**1**), B (**2**), and C (**3**), and a new cucurbitacin glycoside, scrophoside A (**4**), along with two known iridoid glycosides, picrosides I (**5**) (Kitagawa et al., 1971) and II (**6**) (Wang et al., 1993), and three known cucurbitacin glycosides (**7**–**9**) (Stuppner et al., 1991). This paper describes the isolation and structural elucidation of the three new iridoid glycosides and one cucurbitacin glycoside.

2. Results and discussion

Silica gel column chromatography ($CHCl_3$/MeOH 1:0, 50:1, 10:1, 5:1, 1:1 and 0:1) of the EtOAc-soluble portion from a hot MeOH extract of the dried rhizomes of *N. scrophulariiflora*gave 10 fractions. After repeated reversed-phase HPLC using MeOH/H_2O or MeCN/H_2O, fr. 7 afforded a new iridoid glycoside, picroroside C (**3**), a new cucurbitacin glycoside, scrophoside A (**4**), and three known cucurbitacin glycosides (**7**–**9**); fr. 8 afforded two new iridoid glycosides, picrorosides A (**1**) and B (**2**), and picroside I (**5**); and fr. 9 afforded picroside II (**6**). Identification of the known compounds was accomplished by comparison of their spectral data with those in the literature.

Picroroside A (**1**) was obtained as a colorless amorphous powder. Its molecular formula was determined to be $C_{24}H_{30}O_{12}$ by the $[M+H]^+$ quasi-ion peak at *m*/*z* 511.1820 (calcd for $C_{24}H_{31}O_{12}$ 511.1806) in the HR-ESI-MS. The ^1H NMR spectrum of **1** showed the presence of

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two acetal protons [δ 5.58 (*d*, $J = 1.8$), 5.27 (*d*, $J = 3.3$)], two oxygenated methine protons [δ 4.04 (*dd*, $J = 8.2$, 1.4), 4.01 (*dd*, $J = 8.2$, 2.8)], two oxygenated methylene protons [δ 3.95 (*dd*, $J = 11.9$, 1.4), 3.57 (*dd*, $J = 11.9$, 1.8)], two methine protons [δ 2.56 (*br d*, $J = 10.1$), 2.28 (*ddd*, $J = 8.7$, 8.3, 2.8)], two methylene protons [δ 2.43 (*dd*, $J = 13.8$, 8.3), 1.67 (*dd*, $J = 13.8$, 3.3)], five aromatic protons [δ 7.61 (2H), 7.40 (3H)], a pair of *trans* olefinic protons [δ 7.70 (*d*, $J = 16.1$), 6.58 (*d*, $J = 16.1$)], and a monosaccharide group (Table 1). The ^{13}C NMR spectrum of **1** showed the presence of a carbonyl carbon (δ 168.5), an aromatic ring [δ 135.7, 131.6, 130.0 (×2), 129.3 (×2)], two olefinic carbons (δ 146.4, 118.6), and characteristic signals of a glucopyranosyl group (δ 99.1, 78.0, 75.6, 74.6, 71.6, 64.8), in addition to the aglycone moiety containing nine carbon signals (Table 1). The HMBC correlation between H-1′ and C-1 demonstrated that the glucosyl moiety was connected to the C-1 oxygen atom (Fig. 2). The relatively large J value (7.8 Hz) of the anomeric proton (δ 4.72) of the glucosyl moiety indicated that the glucoside linkage was β. The HMBC correlation between H_2-6′ and the carbonyl carbon, and the downfield shift of the oxygenated methylene protons at δ 4.51 and 4.37 (H_2-6′) suggested that the *E*-cinnamoyl group was attached at C-6′ of the glucose moiety (Fig. 2). The ^{1}H and ^{13}C NMR spectra of **1** generally resembled that of **5** indicating that **1** was an iridoid glycoside. However, analysis of the ^{1}H and ^{13}C NMR, H–H COSY and HMBC spectra revealed that **1** has a rigid three ring skeleton. The HMBC correlations between H-3 and C-10, H-7 and C-10, and H-9 and C-10, and the NOESY correlation between H-10b and H-1 indicated that the methylenoxy linkage between C-3 and C-8 had an

Table 1
^{1}H and ^{13}C NMR spectral data for compounds **1**, **2** and **3** in CD_3OD[a]

Position	**1**[b]		**2**[c]		**3**[c]	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	93.5	5.58 (*d*, 1.8)	93.5	5.60 (*d*, 2.1)	93.3	5.59 (*d*, 2.1)
3	95.9	5.27 (*d*, 3.3)	96.0	5.33 (*d*, 3.3)	95.9	5.31 (*d*, 3.5)
4α	34.8	1.67 (*dd*, 13.8, 3.3)	34.8	1.76 (*dd*, 13.8, 3.3)	34.8	1.73 (*dd*, 13.8, 3.5)
4β		2.43 (*dd*, 13.8, 8.3)		2.50 (*m*)		2.48 (*dd*, 13.8, 9.0)
5	35.9	2.28 (*ddd*, 8.7, 8.3, 2.8)	35.0	2.33 (*m*)	34.8	2.31 (*ddd*, 9.4, 9.0, 2.9)
6	84.5	4.01 (*dd*, 8.2, 2.8)	83.1	4.13 (*dd*, 6.9, 2.9)	82.8	4.09 (*dd*, 6.9, 2.9)
7	74.7	4.04 (*dd*, 8.2, 1.4)	87.4	5.38 (*d*, 6.9)	87.0	5.33 (*d* 6.9)
8	79.9		80.1		79.7	
9	48.0	2.56 (*br d*, 10.1)	47.5	2.74 (*br d*, 10.2)	47.3	2.71 (*br d*, 10.0)
10a	62.2	3.95 (*dd*, 11.9, 1.4)	62.0	3.91 (*d*, 12.0)	61.8	3.88 (*d*, 12.1)
10b		3.57 (*dd*, 11.9, 1.8)		3.63 (*d*, 12.0)		3.60 (*dd*, 12.1, 1.2)
1′	99.1	4.72 (*d*, 7.8)	99.0	4.74 (*d*, 8.0)	98.9	4.74 (*d*, 8.0)
2′	74.6	3.21 (*dd*, 9.1, 7.8)	74.7	3.23 (*m*)	74.6	3.23 (*dd*, 9.2, 8.0)
3′	78.0	3.38 (*m*)	78.0	3.40 (*m*)	77.9	3.39 (*m*)
4′	71.6	3.40 (*m*)	71.6	3.41 (*m*)	71.4	3.41 (*m*)
5′	75.6	3.55 (*m*)	75.5	3.57 (*m*)	75.5	3.56 (*m*)
6′a	64.8	4.52 (*dd*, 11.9, 1.8)	64.7	4.53 (*dd*, 12.0, 2.1)	64.6	4.53 (*dd*, 12.0, 2.3)
6′b		4.33 (*dd*, 11.9, 5.5)		4.34 (*dd*, 12.0, 5.5)		4.34 (*dd*, 12.0, 5.7)
1″	135.7		135.7		135.6	
2″	129.3	7.61 (–[d])	129.3	7.62 (–[d])	129.2	7.62 (–[d])
3″	130.0	7.40 (–[d])	130.0	7.39 (–[d])	129.9	7.42 (–[d])
4″	131.6	7.40 (–[d])	131.5	7.38 (–[d])	131.4	7.39 (–[d])
5″	130.0	7.40 (–[d])	130.0	7.39 (–[d])	129.9	7.42 (–[d])
6″	129.3	7.61 (–[d])	129.3	7.62 (–[d])	129.2	7.62 (–[d])
α	118.6	6.58 (*d*, 16.1)	118.6	6.59 (*d*, 16.0)	118.5	6.59 (*d*, 16.0)
β	146.4	7.70 (*d*, 16.1)	146.6	7.72 (*d*, 16.0)	146.5	7.72 (*d*, 16.0)
CO	168.5		168.5		168.5	
1‴			122.1		135.6	
2‴			113.7	7.59 (*d*, 2.1)	129.2	7.62 (–[d])
3‴			148.9		129.9	7.42 (–[d])
4‴			153.4		131.4	7.39 (–[d])
5‴			116.0	6.85 (*d*, 8.2)	129.9	7.42 (–[d])
6‴			125.3	7.63 (*dd*, 8.2, 2.1)	129.2	7.62 (–[d])
OMe			56.4	3.89 (*s*)		
α					118.5	6.63 (*d*, 16.0)
β					146.7	7.76 (*d*, 16.0)
CO			168.1		168.5	

[a] Multiplicity and J values in Hz are given in parentheses.
[b] Measured at 200 MHz (^{13}C NMR) and 800 MHz (^{1}H NMR).
[c] Measured at 125 MHz (^{13}C NMR) and 500 MHz (^{1}H NMR).
[d] Multiplicity was not determined due to overlapping of the signals.

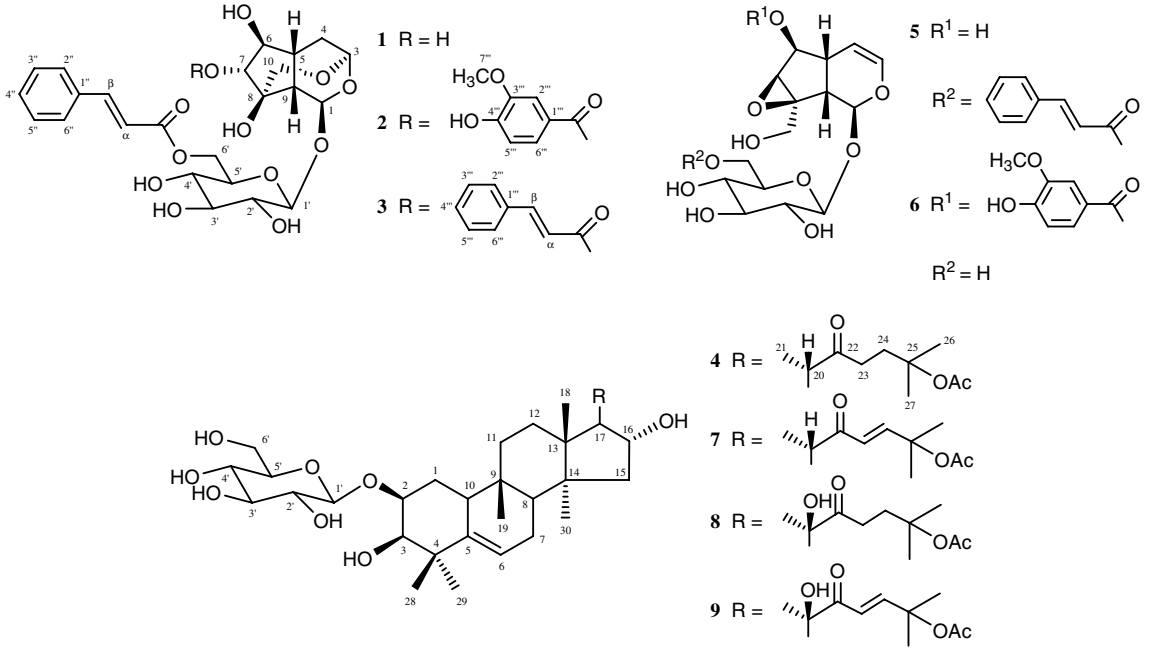

Fig. 1. Structures of picrorosides A (**1**)–C (**3**), scrophoside A (**4**) and related compounds.

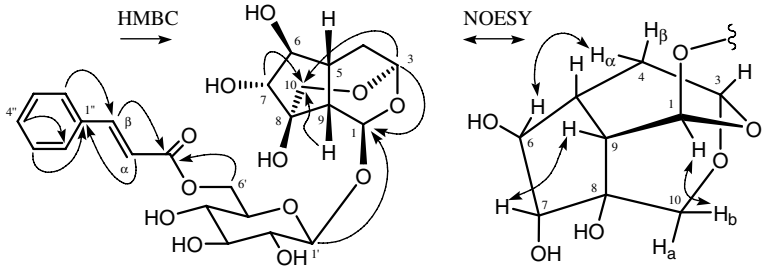

Fig. 2. Selected HMBC and NOESY correlations for 1.

α-configuration (Fig. 2). On the basis of these data, the structure of picroroside A (**1**) was determined to be that shown in Fig. 1.

Picroroside B (**2**) was obtained as a colorless amorphous powder. Its molecular formula was determined to be $C_{32}H_{36}O_{15}$ by the $[M+H]^+$ quasi-ion peak at *m/z* 661.2106 (calcd for $C_{32}H_{37}O_{15}$ 661.2132) in the HR-ESI-MS. The ^{1}H NMR spectrum of **2** showed the presence of two acetal protons [δ 5.60 (*d*, $J=2.1$), 5.33 (*d*, $J=2.9$)], two oxygenated methine protons [δ 5.38 (*d*, $J=6.9$), 4.13 (*dd*, $J=6.9$, 2.9)], two oxygenated methylene protons [δ 3.91 (*d*, $J=12.0$), 3.63 (*d*, $J=12.0$)], two methine protons [δ 2.74 (*br d*, $J=10.2$), 2.33 (*m*)], two methylene protons [δ 2.50 (*m*), 1.76 (*dd*, $J=13.8$, 3.3)], eight aromatic protons (δ 7.63–6.85), a pair of *trans* olefinic protons [δ 7.72 (*d*, $J=16.0$), 6.59 (*d*, $J=16.0$)], a methoxy group (δ 3.89), and a monosaccharide group (Table 1). The ^{13}C NMR spectrum of **2** showed the presence of two carbonyl carbons (δ 168.5, 168.1), 14 olefinic carbons (δ 153.4–113.7), a methoxy group (δ 56.4), and characteristic signals of a glucopyranosyl group (δ 99.0, 78.0, 75.5, 74.7, 71.6, 64.7), in addition to the aglycone moiety containing nine carbon signals (Table 1). The ^{1}H and ^{13}C NMR spectra of **2** were quite similar to those of **1**, except for the signals originating from an aromatic acid moiety, which was determined to be a vanilloyl group by analysis of the ^{13}C NMR (δ 153.4, 148.9, 125.3, 122.1, 116.0, 113.7, 56.4), H–H COSY, and HMBC spectra (Table 1). The HMBC correlation between H-7 and the carbonyl carbon of the vanilloyl group, and the downfield shift of the proton at δ 5.38 (H-7) suggested that the vanilloyl group was attached at C-7 (Fig. 3). Moreover, correlations observed between H-1′ and C-1, and H_2-6′ and the carbonyl carbon of the *E*-cinnamoyl group demonstrated that the glucosyl moiety and the *E*-cinnamoyl group were connected to the C-1 and C-6′ oxygen atom, respectively (Fig. 3). Thus, the structure of picroroside B (**2**) was determined to be that shown in Fig. 1.

Picroroside C (**3**) was obtained as a colorless amorphous powder. Its molecular formula was determined to be $C_{33}H_{36}O_{13}$ by the $[M+H]^+$ quasi-ion peak at *m/z* 641.2220 (calcd for $C_{33}H_{37}O_{13}$ 661.2234) in the HR-ESI-MS. The ^{1}H and ^{13}C NMR spectra of **3** were also quite similar to those of **1**, except for the signals originating from the phenylpropanoid ester moiety, which was determined

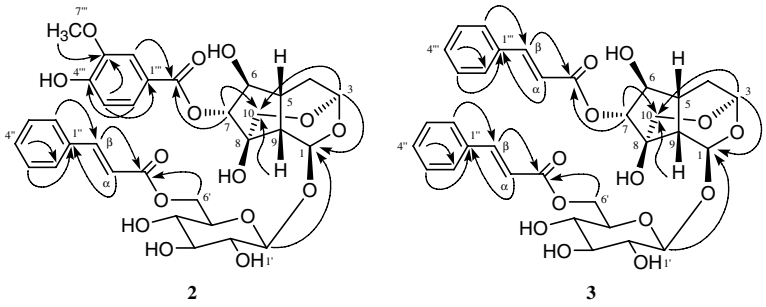

Fig. 3. Selected HMBC correlations for 2 and 3.

to be an *E*-cinnamoyl group by analysis of the ^{13}C NMR [δ 168.5, 146.7, 135.6, 131.4, 129.9 (×2), 129.2 (×2), 118.5], H–H COSY, and HMBC spectra (Table 1). The HMBC correlation between H-7 and the carbonyl carbon of the *E*-cinnamoyl group, and the downfield shift of the proton at δ 5.33 (H-7) suggested that the *E*-cinnamoyl group was attached at C-7 (Fig. 3). Thus, the structure of picroroside C (**3**) was determined to be that shown in Fig. 1.

Scrophoside A (**4**) was obtained as a colorless amorphous powder. Its molecular formula was determined to be $C_{38}H_{62}O_{11}$ by the $[M + Na]^+$ quasi-ion peak at *m/z* 717.4204 (calcd for $C_{38}H_{62}O_{11}Na$ 717.4190) in the HR-ESI-MS. Its ^1H NMR spectrum showed resonances of a secondary methyl (δ 1.12), eight tertiary methyls [δ 1.94, 1.43 (×2), 1.18, 1.08, 1.03, 0.94, 0.93], an olefinic proton (δ 5.58), and a monosaccharide group. The ^{13}C NMR spectrum of **1** showed the presence of eight methyls [δ 28.4, 27.4, 26.2 (×3), 19.0, 17.4, 17.1], seven methylenes (δ 47.5, 37.0, 35.6, 32.8, 31.5, 29.0, 25.4), an acetoxy group (δ 172.5, 22.3), a carbonyl carbon (δ 217.6), two olefinic carbons (δ 141.7, 121.5), five quaternary carbons (δ 83.1, 49.5, 48.8, 42.2, 35.6), and characteristic signals of a glucopyranosyl group (δ 102.0, 78.1, 77.9, 75.2, 71.7, 62.8). The HMBC correlation between H-1′ and C-2 demonstrated that the glucosyl moiety was connected to the C-2 oxygen atom. The relatively large *J* value (7.8 Hz) of the anomeric proton (δ 4.42) of the glucosyl moiety indicated that the glucoside linkage was β. The ^1H and ^{13}C NMR spectra of **4** were quite similar to those of **7**, with all the resonances from the basic structure of **4** having corresponding signals in the spectrum of **7**, suggesting that **4** had basically the same structure as **7** and that the difference was only in the side chain at C-17. Analysis of the ^{13}C NMR, H–H COSY and HMBC spectra revealed that **4** possessed two methylenes at C-23 and C-24, whereas **7** had a double bond between C-23 and C-24 in the side chain (Fig. 4). Accordingly, the structure of scrophoside A (**4**) was determined to be that shown in Fig. 1.

Though similar iridoids with a rigid three ring skeleton have been reported (Iwagawa et al., 1991; Jia et al., 1999; Yoshikawa et al., 1986), picrorosides A, B and C are the first examples of iridoid glycosides having a rigid three ring skeleton from *N.scrophulariiflora*.

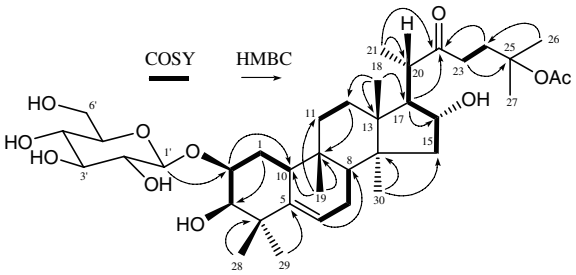

Fig. 4. Selected COSY and HMBC correlations for 4.

3. Experimental

3.1. General

Optical rotations were measured on a JASCO DIP-370 (Tokyo, Japan) digital polarimeter, UV spectra on a Shimadzu UV-2550 (Kyoto, Japan) spectrophotometer and IR spectra on a JASCO FTIR-5300 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in CD_3OD on JEOL ECA-500 and ECA-800 (Tokyo, Japan) spectrometers, and chemical shifts were expressed in parts per million (ppm) relative to TMS as the internal standard. Mass spectra were obtained on a JEOL JMS-T100LC spectrometer. Preparative HPLC was carried out on a Shimadzu LC-8A with a Shimadzu SPD-6AV detector and a reversed-phase column, Wakosil 25C 18 column (20 mm i.d. ×250 mm, ODS, 10 μm, Wako) or Capcell Pak C_{18} column (20 mm i.d. ×250 mm, ODS, 5 μm, Shiseido).

3.2. Plant material

The rhizomes of *N. scrophulariiflora* were purchased from Uchida Wakanyaku Co. Ltd. A voucher specimen was deposited in the National Institute of Health Sciences, Japan.

3.3. Extraction and isolation

The dried and ground rhizomes of *N. scrophulariiflora* (300 g) were extracted with hot MeOH (5 × 500 mL). The solvent was removed in vacuo to give a residue (73.8 g), which was suspended in H_2O (500 mL). The suspension

was extracted with CH_2Cl_2 (3 × 500 mL), EtOAc (3 × 500 mL), and 1-BuOH (3 × 500 mL), successively, and the solvent was removed in vacuoto afford CH_2Cl_2-soluble (6.3 g), EtOAc-soluble (8.9 g), and 1-BuOH-soluble (24.8 g) portions, respectively. The EtOAc-soluble portion was placed on a silica gel column and eluted sequentially with $CHCl_3$/MeOH mixtures (1:0, 50:1, 10:1, 5:1, 1:1 and 0:1) to give 10 fractions (frs. 1–10). Fraction 7 (857.6 mg) was further separated by reversed-phase HPLC using MeOH/H_2O (60:40 and 1:0) to afford five fractions (frs. 7A–7E). Repeated reversed-phase HPLC of fraction 7D (189.1 mg) using mixtures of either MeOH/H_2O or MeCN/H_2O afforded compounds **8** (18.1 mg) and **9** (140.6 mg). Repeated reversed-phase HPLC of fraction 7E (140.1 mg) using mixtures of either MeOH/H_2O or MeCN/H_2O afforded compounds **3** (0.9 mg), **4** (1.2 mg) and **7** (2.4 mg). Fraction 8 (2.46 g) was further separated by reversed-phase HPLC using MeOH/H_2O (38:62 and 1:0) into four sub-fractions (frs. 8A–8D), which were evaporated to dryness. Fraction 8C (287.5 mg) was pure picroside I (**5**). After reversed-phase HPLC using MeOH/H_2O or MeCN/H_2O, fraction 8D (409.3 mg) afforded compounds **1** (11.2 mg) and **2** (1.5 mg). Fraction 9 (1.9 g) was further subjected to reversed-phase HPLC using MeOH/H_2O (34:66 and 1:0) to afford five sub-fractions (frs. 9A–9E). After removal of the solvent, reversed-phase HPLC of fraction 9C (67.3 mg) using MeCN/H_2O (15:85) afforded picroside II (**6**, 56.6 mg).

3.4. Picroroside A (1)

Colorless amorphous powder; $[\alpha]_D^{24}$ −56.3° (*c* 1.12, MeOH); UV (MeOH) λ_{max} nm (logε): 277 (4.32), 217 (4.21); IR (KBr) ν_{max} cm^{-1}: 3434, 1701, 1636; for ^{1}H and ^{13}C NMR spectra, see Table 1; HR-ESI-MS *m*/*z* 511.1820 $[M + H]^+$ (calcd for $C_{24}H_{31}O_{12}$ 511.1806).

3.5. Picroroside B (2)

Colorless amorphous powder; $[\alpha]_D^{24}$ −46.7° (*c* 0.15, MeOH); UV (MeOH) λ_{max}nm (logε): 269 (4.52), 217 (4.62); IR (film) ν_{max} cm^{-1}: 3428, 1635; for ^{1}H and ^{13}C NMR spectra, see Table 1; HR-ESI-MS *m*/*z* 661.2106 $[M + H]^+$ (calcd for $C_{32}H_{37}O_{15}$ 661.2132).

3.6. Picroroside C (3)

Colorless amorphous powder; $[\alpha]_D^{24}$ −44.4° (*c* 0.09, MeOH); UV (MeOH) λ_{max} nm (logε): 278 (4.81), 217 (4.79); IR (film) ν_{max} cm^{-1}: 3380, 1705, 1636; for ^{1}H and ^{13}C NMR spectra, see Table 1; HR-ESI-MS *m*/*z* 641.2220 $[M + H]^+$ (calcd for $C_{33}H_{37}O_{13}$ 641.2234).

3.7. Scrophoside A (4)

Colorless amorphous powder; $[\alpha]_D^{24}$ −33.3° (*c* 0.12, MeOH); UV (MeOH) λ_{max} nm (logε): 279 (3.59); IR (film) ν_{max} cm^{-1}: 3410, 2928, 1717, 1262; ^{1}H NMR (800 MHz, CD_3OD): δ 5.58 (1H, *d*, *J* = 5.9 Hz, H-6), 4.42 (1H, *d*, *J* = 7.8 Hz, H-1′), 4.20 (1H, *m*, H-2), 3.99 (1H, *t*, *J* = 7.8 Hz, H-16), 3.89 (1H, *dd*, *J* = 11.9, 2.2 Hz, H-6′a), 3.66 (1H, *dd*, *J* = 11.9, 6.0 Hz, H-6′b), 3.60 (1H, *br s*, H-3), 3.37 (1H, *dd*, *J* = 9.2, 8.7 Hz, H-3′), 3.30 (1H, *m*, H-5′), 3.27 (1H, *d*, *J* = 8.7 Hz, H-4′), 3.18 (1H, *dd*, *J* = 9.2, 7.8 Hz, H-2′), 2.71 (1H, *m*, H-20), 2.68 (1H, *m*, H-23a), 2.56 (1H, *m*, H-23b), 2.45 (1H, *m*, H-10), 2.40 (1H, *m*, H-7a), 2.03 (1H, *dd*, *J* = 10.6, 6.4 Hz, H-17), 1.98 (2H, *m*, H-24a and H-24b), 1.94 (3H, *s*, OCO*Me*), 1.94 (1H, *m*, H-12a), 1.84 (1H, *m*, H-7b), 1.77 (1H, *m*, H-1a), 1.76 (1H, *m*, H-8), 1.73 (1H, *m*, H-11a), 1.72 (1H, *m*, H-15a), 1.65 (1H, *d*, *J* = 12.4 Hz, H-1b), 1.50 (1H, *m*, H-11b), 1.47 (1H, *m*, H-12b), 1.43 (6H, *s*, H-26 and H-27), 1.26 (1H, *d*, *J* = 12.8 Hz, H-15b), 1.18 (3H, *s*, H-29), 1.12 (3H, *d*, *J* = 6.7 Hz, H-21), 1.08 (3H, *s*, H-30), 1.03 (3H, *s*, H-28), 0.94 (3H, *s*, H-19), 0.93 (3H, *s*, H-18); ^{13}C NMR (200 MHz, CD_3OD): δ 217.6 (C-22), 172.5 (O*CO*Me), 141.7 (C-5), 121.5 (C-6), 102.0 (C-1′), 83.1 (C-25), 78.1 (C-5′), 77.9 (C-3′), 77.5 (C-16), 77.5 (C-2), 77.1 (C-3), 75.2 (C-2′), 71.7 (C-4′), 62.8 (C-6′), 58.0 (C-17), 50.3 (C-20), 49.5 (C-14), 48.8 (C-13), 47.5 (C-15), 44.9 (C-8), 42.2 (C-4), 38.0 (C-10), 37.0 (C-23), 35.6 (C-24), 35.6 (C-9), 32.8 (C-11), 31.5 (C-12), 29.0 (C-1), 28.4 (C-19), 27.4 (C-28), 26.2 (C-29), 26.2 (C-27), 26.2 (C-26), 25.4 (C-7), 22.3 (OCO*Me*), 19.0 (C-30), 17.4 (C-18), 17.1 (C-21); HR-ESI-MS *m*/*z* 717.4204 $[M + Na]^+$ (calcd for $C_{38}H_{62}O_{11}Na$ 717.4190).

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