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ORIGINAL PAPER

Four novel furanocoumarin glucosides, candinosides A, B, C and D, from *Heracleum candicans* Wall

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Abstract Four novel furanocoumarin glucosides, candinosides A, B, C and D (**1**–**4**), were isolated from the roots of *Heracleum candicans* Wall. Their structures were established using chemical and spectral methods.

Keywords *Heracleum candicans* · Umbelliferae · Furanocoumarin glucoside

Introduction

The roots of *Heracleum candicans* Wall are used in Chinese folk medicine as an antipyretic and diaphoretic agent in local areas of Yunnan Province, PR China [1]. In our previous studies, we reported the isolation and structural elucidation of 14 coumarin derivatives, in addition to two known polyacetylenes, two known phenylpropanoids and 25 known coumarins, including heraclenol and marmesin [2–4]. However, the chemical constituents of this plant have not yet been investigated thoroughly. In the course of our studies on the coumarin components of this plant, we investigated the constituents of the high-polarity fractions and isolated four novel furanocoumarin glucosides, candinosides A–D (**1**–**4**), as shown in Fig. 1. This report deals with the isolation and structural elucidation of the four new natural products.

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Results and discussion

The acetone extract of the roots of this plant yielded four new coumarins (**1**–**4**) after chromatographic purification.

Candinoside A (**1**) was obtained as a pale yellow viscous oil, $[\alpha]_D^{25}$ +7.5° (*c* 0.578, pyridine), which presented a fluorescent yellowish-green spot on TLC under UV light (365 nm). The UV spectrum showed absorption maxima at 298.0, 248.0 and 210.5 nm and IR spectrum absorption bands at 3414, 2979, 1718, 1623, 1588, 1468, 1442, 1403, 1334, 1294, 1154 and 1089 cm^{-1}, indicating the presence of linear-type furanocoumarins. The molecular formula was determined as $C_{38}H_{40}O_{16}$ on the basis of high-resolution (HR) positive FAB-MS (*m/z*: 775.2211, $[M + Na]^+$, calcd. 775.2214).

The ^{1}H-NMR spectrum of **1** showed the presence of two heraclenol units [heraclenol unit I: δ_H 7.76 (1H, d, $J = 9.7$ Hz), 7.70 (1H, d, $J = 2.3$ Hz), 7.36 (1H, s), 6.81 (1H, d, $J = 2.3$ Hz), 6.35 (1H, d, $J = 9.7$ Hz), 4.65 (1H, dd, $J = 10.4$, 2.5 Hz), 4.46 (1H, dd, $J = 10.4$, 8.0 Hz), 4.10 (1H, dd, $J = 8.0$, 2.5 Hz), 1.40 (3H, s), 1.34 (3H, s)], [heraclenol unit II: δ_H 7.78 (1H, d, $J = 9.6$ Hz), 7.71 (1H, d, $J = 2.3$ Hz), 7.38 (1H, s), 6.81 (1H, d, $J = 2.3$ Hz), 6.36 (1H, d, $J = 9.6$ Hz), 4.69 (1H, dd, $J = 10.0$, 2.6 Hz), 4.54 (1H, dd, $J = 10.0$, 8.8 Hz), 4.00 (1H, dd, $J = 8.8$, 2.6 Hz), 1.47 (3H, s), 1.34 (3H, s)] and one glucopyranose unit [δ_H 4.66 (1H, d, $J = 8.0$ Hz), 3.29 (1H, dd, $J = 9.0$, 8.0 Hz), 3.71 (1H, t, $J = 9.0$ Hz), 3.51 (1H, t, $J = 9.0$ Hz), 3.39 (1H, ddd, $J = 9.0$, 5.3, 3.5 Hz), 3.89 (1H, dd, $J = 11.8$, 3.5 Hz), 3.79 (1H, dd, $J = 11.8$, 5.3 Hz)] (Table 1). Each unit was also identified by ^{13}C-NMR spectroscopy (Table 2).

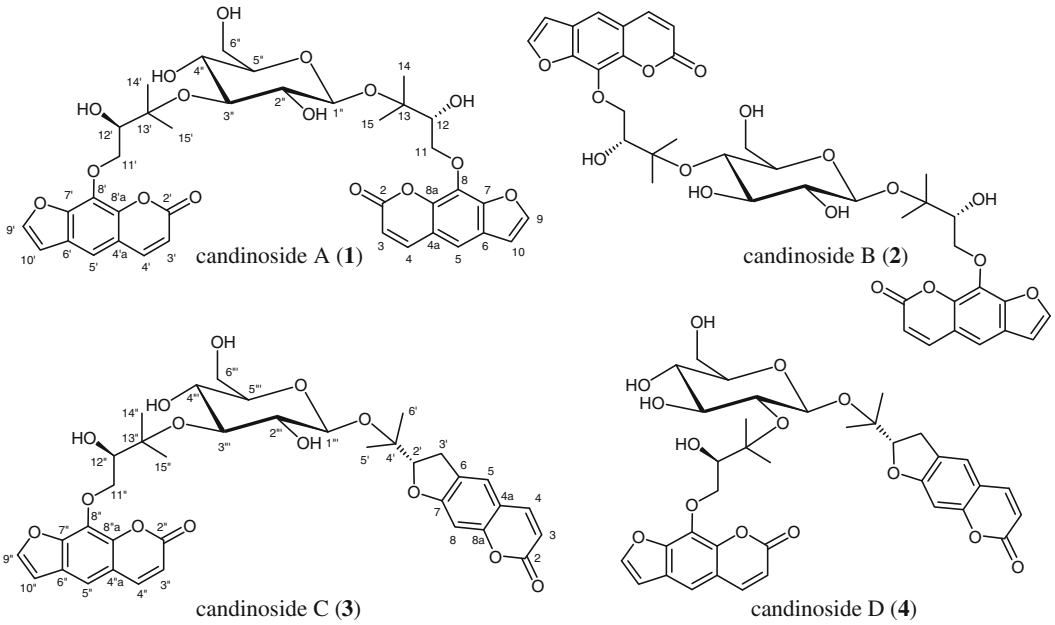

Fig. 1 Structures of **1**–**4**

Table 1 ^{1}H-NMR spectral data for **1**, **2** and heraclenol in $CDCl_3$

	1		2		Heraclenol
3/3′	6.35d (9.7)	6.36d (9.6)	6.33d (9.6)	6.36d (9.7)	6.37d (9.6)
4/4′	7.76d (9.7)	7.78d (9.6)	7.74d (9.6)	7.76d (9.7)	7.76d (9.6)
5/5′	7.36s	7.38s	7.34s	7.35s	7.39s
9/9′	7.70d (2.3)	7.71d (2.3)	7.70d (2.2)	7.72d (2.3)	7.70d (2.3)
10/10′	6.81d (2.3)	6.81d (2.3)	6.79d (2.2)	6.80d (2.3)	6.83d (2.3)
11/11′	4.46dd (10.4, 8.0)	4.54dd (10.0, 8.8)	4.45dd (10.1, 7.6)	4.59dd (10.1, 8.4)	4.42dd (10.2, 7.9)
	4.65dd (10.4, 2.5)	4.69dd (10.0, 2.6)	4.66dd (10.1, 3.0)	4.66dd (10.1, 3.1)	4.75dd (10.2, 2.7)
12/12′	4.10dd (8.0, 2.5)	4.00dd (8.8, 2.6)	4.10dd (7.6, 3.0)	3.91dd (8.4, 3.1)	3.89ddd (7.9, 4.1, 2.7)
14/14′	1.34s	1.34s	1.34s	1.27s	1.31s
15/15′	1.40s	1.47s	1.38s	1.44s	1.34s
12-OH					3.54d (4.1)
13-OH					2.74s
1″	4.66d (8.0)		4.66d (8.0)		
2″	3.29dd (9.0, 8.0)		3.44dd (8.7, 8.0)		
3″	3.71t (9.0)		3.65t (8.7)		
4″	3.51t (9.0)		3.70t (8.7)		
5″	3.39ddd (9.0, 5.3, 3.5)		3.29ddd (8.7, 5.5, 2.6)		
6″	3.89dd (11.8, 3.5)		3.83dd (11.8, 2.6)		
	3.79dd (11.8, 5.3)		3.70dd (11.8, 5.5)		

Chemical shifts are in δ values and are followed by multiplicities and J values (in Hz)

In the heteronuclear multiple bond correlation (HMBC) spectrum of **1**, the anomeric proton signal of δ_H 4.66 (H-1″, glucopyranose unit) was correlated with the carbon signal of δ_c 78.9 (C-13, heraclenol unit I), and δ_H 1.34 (H-14, heraclenol unit I) and δ_H 1.40 (H-15, heraclenol unit I) with δ_c 97.1 (C-1″, glucopyranose unit); δ_H 3.71 (H-3″, glucopyranose unit) with δ_c 77.9 (C-13′, heraclenol unit II) (Fig. 2). Thus, **1** was assumed to be a furanocoumarin glucoside composed of two heraclenol units and a glucopyranose unit, and the two heraclenol units were found to be located at the C-1″ and C-3″ positions in the glucopyranose unit. The structure has an ether bond at C-3″ of the glucopyranose unit and a novel glycosidic bond. Previously, the absolute configuration of the C-12 position of heraclenol

Table 2 ^{13}C-NMR spectral data for **1**, **2** and heraclenol in $CDCl_3$

	1		2		Heraclenol
2/2′	160.6	160.9	160.6	160.9	160.1
3/3′	114.5	114.4	114.5	114.4	114.7
4/4′	144.5	144.8	144.5	144.7	144.3
4a/4a′	116.4	116.4	116.4	116.4	116.4
5/5′	113.6	113.7	113.49[d]	113.51[d]	113.7
6/6′	126.0	126.1	126.07[e]	126.15[e]	126.0
7/7′	148.1[a]	148.2[a]	148.0[f]	148.1[f]	147.9
8/8′	131.68[b]	131.71[b]	131.79[g]	131.74[g]	131.5
8a/8a′	143.34	143.28	143.24	143.20	143.2
9/9′	146.85	146.94	146.86	146.93	146.8
10/10′	106.76[c]	106.78[c]	106.72[h]	106.75[h]	106.8
11/11′	75.1	75.1	75.1	75.0	75.7
12/12′	75.4	77.1	75.4	77.4	76.0
13/13′	78.9	77.9	78.9	78.5	71.5
14/14′	23.6	25.0	23.3	26.5	25.0
15/15′	22.8	24.0	22.92[i]	22.86[i]	26.6
1″	97.1		96.6		
2″	73.8		74.1		
3″	78.0		77.0		
4″	71.2		71.3		
5″	75.6		76.1		
6″	62.9		62.0		

Chemical shifts are in δ values

[a–i] Assignment may be reversed

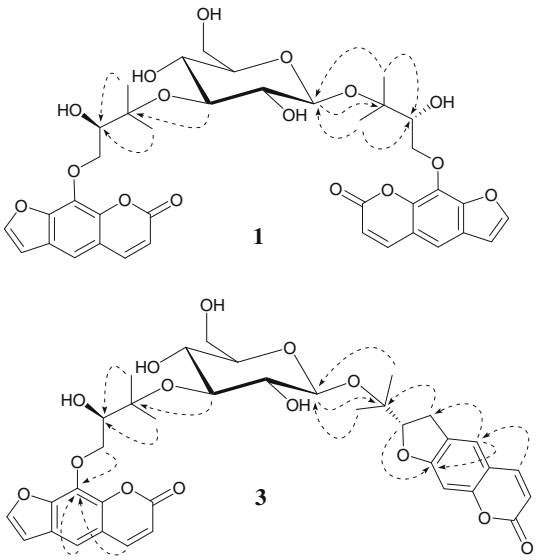

Fig. 2 Main HMBC correlations of **1** and **3**

was found to be *R* using the modified Mosher's method [5]. Although we made no attempt to determine it directly, the configuration of the C-12 and C-12′ positions of **1** was also assumed to be *R*, similar to heraclenol. Thus, the structure of candinoside A (**1**) was found to be that shown in Fig. 1. This structure was supported by analyses of the ^{1}H-^{1}H COSY, HMQC, HMBC and NOESY spectra of **1**.

Candinoside B (**2**) was obtained as a pale yellow viscous oil, $[\alpha]_D^{25}$ +30.8° (*c* 0.857, pyridine), which presented a fluorescent yellowish-green spot on TLC under UV light (365 nm). The UV spectrum showed absorption maxima at 298.0, 248.0 and 210.5 nm and IR spectrum absorption bands at 3424, 2979, 1717, 1623, 1588, 1468, 1442, 1403, 1334, 1294, 1153 and 1095 cm^{-1}, indicating the presence of linear-type furanocoumarins. The molecular formula was found to be $C_{38}H_{40}O_{16}$ on the basis of HR positive FAB-MS (*m/z*: 775.2217, $[M + Na]^+$, calcd. 775.2214).

The ^{1}H-NMR and ^{13}C-NMR spectral data (Tables 1, 2) were very similar to those of **2**, showing the presence of two heraclenol units and one glucopyranose unit.

Upon analyzing the HMBC spectral data, three-bond correlations were observed between the anomeric proton signal of δ_H 4.66 (H-1‴, glucopyranose unit) and the carbon signal of δ_c 78.9 (C-13, heraclenol unit I), and δ_H 1.34 (H-14, heraclenol unit I) and δ_H 1.38 (H-15, heraclenol unit I) and δ_c 96.6 (C-1″, glucopyranose unit); δ_H 3.70 (H-4″, glucopyranose unit) and δ_c 78.5 (C-13′, heraclenol unit II). On the basis of this evidence, the structure of candinoside B (**2**) was elucidated as shown in Fig. 1.

Candinoside C (**3**) was obtained as a pale yellow viscous oil, $[\alpha]_D^{25}$ +76.9° (*c* 0.172, pyridine), which presented a fluorescent yellowish-green spot on TLC under UV light (365 nm). The UV spectrum showed absorption maxima at 300.0, 249.0 and 210.5 nm and IR spectrum absorption bands at 3424, 2901, 1719, 1627, 1400 and 1105 cm^{-1}, indicating the presence of linear-type furanocoumarins. The molecular formula was found to be $C_{36}H_{38}O_{14}$ on the basis of HR positive FAB-MS (*m/z*: 717.2150, $[M + Na]^+$, calcd. 717.2159).

The ^{1}H-NMR spectrum (Table 3) of **3** showed the presence of one heraclenol unit, [δ_H 7.82 (1H, d, $J = 9.6$ Hz), 7.71 (1H, d, $J = 2.2$ Hz), 7.42 (1H, s), 6.84 (1H, d, $J = 2.2$ Hz), 6.39 (1H, d, $J = 9.6$ Hz), 4.67 (1H, dd, $J = 10.2$, 2.7 Hz), 4.58 (1H, dd, $J = 10.0$, 8.9 Hz), 3.97 (1H, dd, $J = 8.9$, 2.7 Hz), 1.49 (3H, s), 1.31 (3H, s)], one marmesin unit [δ_H 7.58 (1H, d, $J = 9.4$ Hz), 7.20 (1H, s), 6.74 (1H, s), 6.21 (1H, d, $J = 9.4$ Hz), 4.81 (1H, dd, $J = 9.4$, 8.2 Hz), 3.22 (2H, m), 1.35 (6H, s)] and one glucopyranose unit [δ_H 4.59 (1H, d, $J = 8.0$ Hz), 3.22 (1H, dd, $J = 9.2$, 8.0 Hz), 3.70 (1H, t, $J = 9.2$ Hz), 3.53 (1H, t, $J = 9.2$ Hz), 3.30 (1H, ddd, $J = 9.2$, 4.9, 3.8 Hz), 3.70 (1H, br.d), 3.62 (1H, br.d)]. Upon analyzing the HMBC spectral data, three-bond correlations were observed between the anomeric proton signal of δ_H 4.59 (H-1‴, glucopyranose unit) and the carbon signal of δ_c 78.6 (C-4′, marmesin unit), and δ_H 3.70 (H-3‴, glucopyranose unit) and δ_c 77.8 (C-13″, heraclenol unit) (Fig. 2). Moreover, the

Table 3 ^{1}H-NMR spectral data of **3**, **4** and marmesin in $CDCl_3$

	3				**4**			Marmesin	
3	6.21d (9.4)	3″	6.39d (9.6)	3	6.20d (9.5)	3″	6.37d (9.6)	3	6.21d (9.4)
4	7.58d (9.4)	4″	7.82d (9.6)	4	7.58d (9.5)	4″	7.79d (9.6)	4	7.60d (9.4)
5	7.20s	5″	7.42s	5	7.20s	5″	7.40s	5	7.22s
8	6.74s	9″	7.71d (2.2)	8	6.71s	9″	7.71d (2.3)	8	6.74s
2′	4.81dd (9.4, 8.2)	10″	6.84d (2.2)	2′	4.86t (8.9)	10″	6.83d (2.3)	2′	4.74dd (9.2, 8.6)
3′	3.22m	11″	4.58dd (10.0, 8.9)	3′	3.23d (8.9)	11″	4.33dd (10.1, 7.7)	3′	3.22m
5′	1.35s		4.67dd (10.0, 2.7)	5′	1.32s		4.68dd (10.0, 2.9)	5′	1.24s
6′		12″	3.97dd (8.9, 2.7)	6′	1.34s	12″	4.11dd (7.7, 2.9)	6′	1.38s
		14″	1.31s			14″	1.32s		
		15″	1.49s			15″	1.39s		
1‴			4.59d (8.0)				4.59d (7.3)		
2‴			3.22dd (9.2, 8.0)				3.59dd (7.3, 9.2)		
3‴			3.70t (9.2)				3.59t (9.2)		
4‴			3.53t (9.2)				3.54t (9.2)		
5‴			3.30ddd (9.2, 4.9, 3.8)				3.31ddd (9.2, 4.5, 4.2)		
6‴			3.62brd				3.64m		
			3.70brd						

Chemical shifts are in δ values and are followed by multiplicities and J values (in Hz)

Table 4 ^{13}C-NMR spectral data of **3**, **4** and marmesin in $CDCl_3$

	3				**4**			Marmesin	
2	161.4	2″	161.0	2	161.4	2″	160.6	2	161.4
3	112.3	3″	114.4	3	112.3	3″	114.6	3	112.2
4	143.6	4″	144.9	4	143.1	4″	144.7	4	143.7
4a	112.7	4a″	116.5	4a	112.7	4a″	116.4	4a	112.7
5	123.2	5″	113.9	5	123.3	5″	113.9	5	123.4
6	124.8	6″	126.2	6	124.7	6″	126.2	6	125.0
7	163.3	7″	148.4	7	163.3	7″	148.1	7	163.1
8	98.0	8″	131.8	8	97.9	8″	131.5	8	97.9
8a	155.7	8a″	143.5	8a	155.7	8a″	143.4	8a	155.6
2′	90.0	9″	147.0	2′	89.8	9″	146.9	2′	91.1
3′	29.9	10″	106.9	3′	30.2	10″	106.9	3′	29.5
4′	78.6	11″	75.1	4′	78.9	11″	75.5	4′	71.6
5′	22.6	12″	77.0	5′	22.1	12″	77.7	5′	26.1
6′	22.5	13″	77.8	6′	22.4	13″	78.4	6′	24.2
		14″	25.7			14″	26.2		
		15″	23.7			15″	20.9		
1‴		97.6				97.4			
2‴		73.7				74.7			
3‴		77.5				77.2			
4‴		71.1				71.4			
5‴		75.5				75.0			
6‴		62.7				62.7			

Chemical shifts are in δ values

acid hydrolysis of **3** gave marmesin, and the optical rotation $[\alpha]_D^{25}$ was +9.58° [6]. It was concluded that the aglycone was not nodakenetin but marmesin. On the basis of this evidence, the structure of candinoside B (**2**) was elucidated as shown in Fig. 1.

Candinoside D (**4**) was obtained as a pale yellow viscous oil, $[\alpha]_D^{25}$ −42.0° (*c* 0.339, pyridine), which presented a fluorescent yellowish-green spot on TLC under UV light (365 nm). The UV spectrum showed absorption maxima at 334.0sh, 300.0, 249.0 and 210.5 nm and IR spectrum absorption bands at 3420, 2894, 1719, 1626, 1588, 1400 and 1099 cm^{-1}, indicating the presence of linear-type furanocoumarins. The molecular formula was found to be $C_{36}H_{38}O_{14}$ on the basis of HR positive FAB-MS (*m/z*: 717.2161, $[M + Na]^+$, calcd. 717.2159).

The ^{1}H-NMR and ^{13}C-NMR spectral data (Tables 3, 4) were very similar to those of **3**, showing the presence of one heraclenol unit, one marmesin unit and one glucopyranose unit. Long-range correlations were observed between the anomeric proton signal of δ_H 4.59 (H-1‴, glucopyranose unit) and the carbon signal of δ_c 78.9 (C-4′, marmesin unit), and δ_H 3.59 (H-2‴, glucopyranose unit) and δ_c 78.4 (C-13″, heraclenol unit). Thus, the structure was formulated as **4** in Fig. 1.

These four new furanocoumarin glucosides, candinosides A–D (**1**–**4**), have interesting structures, with an ether bond at C-2″ or C-3″ or C-4″ of the glucopyranose unit to connect with an aglycone, except for the C-1″ *O*-glycosidic bond. To the best of our knowledge, these novel glucosides are the first reported from natural products. Moreover, since the ether bonds at C-2″, C-3″ or C-4″ of the four new glycosides are as difficult to hydrolyze as *C*-glucoside, their biological activity must be interesting.

Experiments

General

^{1}H- and ^{13}C-NMR, COSY, DEPT, HMQC, HMBC and NOESY spectra were recorded on a Varian Unity INOVA-500 spectrometer (Palo Alto, CA, USA), operating at 500 MHz for proton and 125 MHz for carbon, with tetramethylsilane (TMS) as an internal standard. HR-FAB-MS spectra were obtained using a JEOL MS700V mass spectrometer (Tokyo, Japan). UV and IR spectra were recorded on a Shimadzu UVmini-1240 (Kyoto, Japan) and a JASCO FT/IR-680 Plus spectrophotometer (Osaka, Japan), respectively. ORD spectra were recorded on a JASCO J820 digital polarimeter. Column chromatography was performed using PSQ100B silica gel (Fuji Silycia, Aichi, Japan), YMC GEL ODS-A 60-400/230 (Kyoto, Japan) and Sephadex LH-20 (GE Healthcare Japan, Tokyo, Japan). HPLC was performed using Shimadzu LC-10AT, SPD-10A and SCL-10A LC instruments. TLC and preparative TLC were carried out on Merck silica gel F_{254} plates (Darmstadt, Germany) and Whatmann silica gel 150A PLK 5F (Maidstone, UK), respectively. Spots and bands were detected by UV irradiation (254 and 365 nm).

Plant material

Air-dried roots of *H. candicans* were collected from plants grown in Lijiang, Yunnan Province, PR China, in September 2004. A voucher specimen was deposited at the Institute of Botany, Jiangsu Province, and Academia Sinica, Nanjing, PR China. The plant was identified by one of the authors (N.W.).

Extraction and isolation

The roots (3.5 kg) were chopped into small pieces and extracted with acetone (10 L × 4) at room temperature. The combined acetone extracts were concentrated to dryness in vacuo. The residue (300.2 g) was subjected to column chromatography on silica gel (2.8 kg) using a gradient of mixtures of hexane–EtOAc (2:1 → 1:2), CH_2Cl_2–MeOH (10:1 → 5:1) and MeOH to furnish 11 fractions (fr.) [fr. 1 (5.0 g), fr. 2 (2.3 g), fr. 3 (8.6 g), fr. 4 (47.4 g), fr. 5 (8.9 g), fr. 6 (24.0 g), fr. 7 (3.9 g), fr. 8 (14.9 g), fr. 9 (16.7 g), fr. 10 (48.4 g) and fr. 11 (96.9 g)].

Fraction 9 was rechromatographed on silica gel and ODS (80% MeOH) to give heraclenol (7.1 g) and marmesin (0.34 g). Fraction 10 was rechromatographed on silica gel (CH_2Cl_2–MeOH = 20:1 → 1:1) to furnish 8 fractions (fr. A–fr. H). Fraction F was rechromatographed on Sephadex LH-20 (MeOH) followed by preparative HPLC (column: Nucleosil 5C18 AB, 10 mm i.d. × 250 mm; mobile phase: 55% MeOH; flow rate: 2 mL/min; detection: UV 254 nm) to give candinoside A (**1**) (24.8 mg) and candinoside B (**2**) (16.0 mg). Fraction H was rechromatographed on silica gel with Sephadex LH-20 (MeOH) followed by ODS (80% MeOH) and PTLCs (CH_2Cl_2:MeOH = 6:1 and EtOAc:MeOH = 8:1) to give candinoside C (**3**) (5.1 mg) and candinoside D (**4**) (3.6 mg).

Candinoside A (**1**)

Yellowish viscous oil, HR-FAB-MS (positive mode) *m/z*: 775.2211 $[M + Na]^+$ (calcd. for $C_{38}H_{40}O_{16}Na$: 775.2214), FAB-MS *m/z* (rel. int.): 775 $[M + Na]^+$ (9), 753 (3), 449 (22), 287 (100), 269 (32), 202 (56). $[\alpha]_D^{25}$ +7.5° (*c* 0.578, pyridine). IR (KBr) cm^{-1}: 3414, 2979, 1718, 1623, 1588, 1468, 1442, 1403, 1334, 1294, 1154, 1089, 1034. UVλ_{max} (MeOH:dioxane = 1:1) nm (log ε): 298.0 (4.12), 248.0 (4.42), 210.5 (4.53). ^{1}H- and ^{13}C-NMR data are shown in Tables 1 and 2.

Candinoside B (**2**)

Yellowish viscous oil, HR-FAB-MS (positive mode) *m/z*: 775.2217 $[M + Na]^+$ (calcd. for $C_{38}H_{40}O_{16}Na$: 775.2214), FAB-MS *m/z* (rel. int.): 775 $[M + Na]^+$ (69), 753 (2), 449 (24), 287 (100), 269 (32), 202 (58). $[\alpha]_D^{25}$ +30.8° (*c* 0.857, pyridine). IR (KBr) cm^{-1}: 3424, 2979, 1717, 1623, 1588, 1468, 1442, 1403, 1334, 1294, 1153, 1095. UVλ_{max} (MeOH:dioxane = 1:1) nm (log ε): 298.0 (4.43), 248.0 (4.72), 210.5 (4.82). ^{1}H- and ^{13}C-NMR data are shown in Tables 1 and 2.

Candinoside C (**3**)

Yellowish viscous oil, HR-FAB-MS (positive mode) *m/z*: 717.2150 $[M + Na]^+$ (calcd. for $C_{36}H_{38}O_{14}Na$: 717.2159), FAB-MS *m/z* (rel. int.): 717 $[M + Na]^+$ (2), 449 (1), 287 (4), 221 (14), 147 (34). $[\alpha]_D^{25}$ +76.9° (*c* 0.172, pyridine). IR (KBr) cm^{-1}: 3424, 2901, 1719, 1627, 1400, 1105. UVλ_{max} (MeOH:dioxane = 1:1) nm (log ε): 300.0 (4.21), 249.0 (4.46), 210.5 (4.60). ^{1}H- and ^{13}C-NMR data are shown in Tables 3 and 4.

Acid hydrolysis of 3

3 (3.1 mg) was dissolved in 3.0% HCl:MeOH = 1:1 (5 mL) and heated in a water bath at 85°C for 2 h. The reaction mixture was diluted with water and then extracted with EtOAc. The EtOAc layer was chromatographed on PTLC (CH_2Cl_2:MeOH = 30:1) to give marmesin (1.1 mg). The optical rotation was $[\alpha]_D^{25}$ + 9.58° (*c* 0.110,

$CHCl_3$). The ^{1}H- and ^{13}C-NMR data (Tables 3, 4) were identical to those reported in the literature [7].

Candinoside D (4)

Yellowish viscous oil, HR-FAB-MS (positive mode) *m/z*: 717.2161 $[M + Na]^+$ (calcd. for $C_{36}H_{38}O_{14}Na$: 717.2159), FAB-MS *m/z* (rel. int.): 717 $[M + Na]^+$ (4), 449 (15), 287 (41), 269 (22), 203 (56), 124 (100). $[\alpha]_D^{25}$ −42.0° (*c* 0.339, pyridine). IR (KBr) cm^{-1}: 3420, 2894, 1719, 1626, 1588, 1400, 1099. UVλ_{max} (MeOH:dioxane = 1:1) nm (log ε): 334.0sh (4.08), 300.0 (4.12), 249.0 (4.32), 210.5 (4.52). ^{1}H- and ^{13}C-NMR data are shown in Tables 3 and 4.

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