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## PETIOLINS D AND E, PHLOROGLUCINOL DERIVATIVES FROM *HYPERICUM PSEUDOPETIOLATUM* VAR. *KIUSIANUM*

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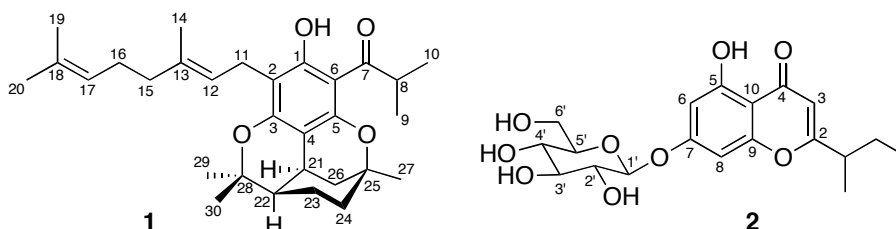
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**Abstract** - A new phloroglucinol derivative possessing citran skeleton, petiolin D (**1**), and a new chromone glucoside, petiolin E (**2**), were isolated from aerial parts of *Hypericum pseudopetiolum* var. *kiusianum*. The structures of **1** and **2** were elucidated by spectroscopic data, and a single-crystal X-ray diffraction analysis of **1** revealed that **1** was a racemic mixture.

### INTRODUCTION

The plants, belonging to the genus *Hypericum* (family Clusiaceae), are known to be a traditional medicine for the treatment of burns, bruises, swelling, inflammation, and anxiety as well as bacterial and viral infections.<sup>1-4</sup> In our continuing search for bioactive compounds from *Hypericum* spp,<sup>5-10</sup> we previously isolated new phloroglucinol derivatives, petiolins A – C, from the aerial parts of *Hypericum pseudopetiolum* var. *kiusianum*.<sup>11</sup> Further investigation of extracts from this plant resulted in the isolation of a new phloroglucinol derivative possessing citran skeleton, petiolin D (**1**), and a new chromone glucoside, petiolin E (**2**), were isolated from aerial parts of *H. pseudopetiolum* var. *kiusianum*. In this paper, we describe the isolation and structure elucidation of **1** and **2**.



## RESULTS AND DISCUSSION

The aerial parts of *H. pseudopetiolum* var. *kiusianum* were extracted with MeOH, and the extracts were partitioned successively with *n*-hexane, EtOAc, and H<sub>2</sub>O. *n*-Hexane-soluble portions were subjected to a silica gel column (*n*-hexane/EtOAc) and then a Sephadex LH-20 column (EtOH) chromatographies to afford a mixture of phloroglucinol derivatives, which was purified by a C<sub>18</sub> column (MeOH/H<sub>2</sub>O) and C<sub>18</sub> HPLC (MeOH/H<sub>2</sub>O) to yield petiolin D (**1**, 0.0008%). EtOAc-soluble portions were applied to a Sephadex LH-20 column (MeOH/H<sub>2</sub>O), a C<sub>18</sub> column (MeOH/H<sub>2</sub>O), a silica gel column (CHCl<sub>3</sub>/MeOH) chromatographies, and C<sub>18</sub> HPLC (MeOH/H<sub>2</sub>O) to give petiolin E (**2**, 0.0008%).

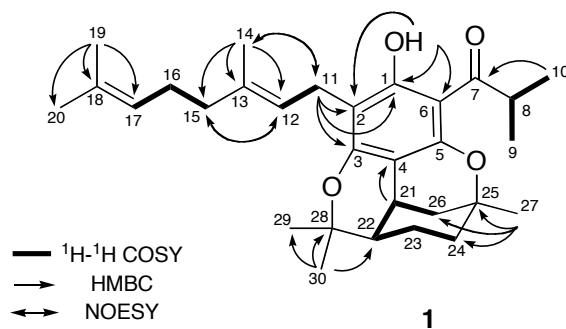
The molecular formula of petiolin D (**1**), C<sub>30</sub>H<sub>42</sub>O<sub>4</sub>, was established by HRESIMS [ $m/z$  489.2973 (M+Na)<sup>+</sup>,  $\Delta$  -0.8 mmu]. <sup>1</sup>H and <sup>13</sup>C NMR data (Table 1) of **1** revealed the presence of one hydrogen-bonded hydroxyl ( $\delta_{\text{H}}$  14.07), one fully substituted benzene ring ( $\delta_{\text{C}}$  163.1, 160.4, 156.0, 110.8, 106.0, and 104.9), two trisubstituted olefins [ $\delta_{\text{H}}$  5.20 and 5.08 (each 1H, t,  $J$  = 7.0 Hz);  $\delta_{\text{C}}$  134.2, 131.0, 124.5, and 122.9], one 2-methylpropanoyl group [ $\delta_{\text{H}}$  3.79 (1H, sept,  $J$  = 6.5 Hz), 1.19 and 1.18 (each 3H, d,  $J$  = 6.5 Hz);  $\delta_{\text{C}}$  209.8, 38.9, 19.6, and 19.1], two sp<sup>3</sup> quaternary carbons attached to an oxygen atom [ $\delta_{\text{C}}$  84.5 and 75.9], two methines [ $\delta_{\text{H}}$  2.82 (1H, brs) and 2.20 (1H, m);  $\delta_{\text{C}}$  45.9 and 27.6], three methylenes [ $\delta_{\text{H}}$  2.18 (1H, ddd,  $J$  = 13.2, 4.4, 3.0 Hz), 1.86 (1H, dd,  $J$  = 13.2, 1.5 Hz), 1.82, 1.47, 1.32, 0.90 (each 1H, m);  $\delta_{\text{C}}$  37.4, 34.8, and 21.9], and three tertiary methyl groups [ $\delta_{\text{H}}$  1.55, 1.43, and 1.06 (each 3H, s);  $\delta_{\text{C}}$  29.6, 28.7, and 24.2]. The presence of a geranyl group was implied by <sup>1</sup>H-<sup>1</sup>H COSY correlations of H<sub>2</sub>-11 to H-12 and H<sub>2</sub>-15 to H-17, HMBC correlations of H<sub>3</sub>-14 to C-12, C-13, and C-15, H<sub>3</sub>-19 to C-17, C-18, and C-20, and NOESY correlations of H<sub>2</sub>-11 to H<sub>3</sub>-14 and H-12 to H<sub>2</sub>-15. The <sup>1</sup>H-<sup>1</sup>H COSY spectrum suggested the connectivity of C-24 to C-26. HMBC correlations of H<sub>3</sub>-27 to C-24, C-25, and C-26 indicated that an oxygenated sp<sup>3</sup> quaternary carbon (C-25) was attached to C-24, C-26, and C-27. Connectivities of C-28 to C-22, C-29, and C-30 were deduced from HMBC correlations of H<sub>3</sub>-30 to C-22, C-28, and C-29. <sup>13</sup>C NMR chemical shifts of a benzene ring suggested the 1,3,5-trihydroxy substitution. HMBC correlations of H<sub>2</sub>-11 to C-1, C-2, and C-3, and H-21 to C-4 indicated that C-11 and C-21 were attached to C-2 and C-4, respectively (Figure 1). The molecular formula and the unsaturation degree of **1** implied that C-3 and C-5 were connected to C-25 or C-28 through an ether linkage, respectively.

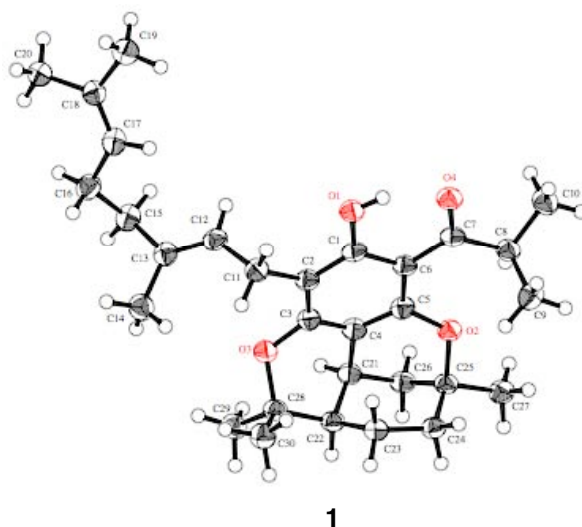
Petiolin D (**1**) was crystallized from methanol/water as colorless platelets. A single-crystal X-ray diffraction analysis of **1** revealed the structure and relative stereochemistry. This crystal consisted of a pair of enantiomers, suggesting that **1** was a racemate. The ORTEP drawing of one enantiomer of **1** was shown in Figure. 2. Thus, the structure of petiolin D was elucidated to be **1**, a new phloroglucinol derivative possessing citran skeleton.

**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data for Petiolin D (**1**) in  $\text{CDCl}_3$ .

position	$^{13}\text{C}$	$^1\text{H}^a$
1	163.1	-
2	110.8	-
3	160.4	-
4	106.0	-
5	156.0	-
6	104.9	-
7	209.8	-
8	38.9	3.79 (1H, sept, $J = 6.5$ Hz)
9	19.1	1.19 (3H, d, $J = 6.5$ Hz)
10	19.6	1.18 (3H, d, $J = 6.5$ Hz)
11	21.2	3.26, 3.22 (each 1H, dd, $J = 14.3, 7.0$ Hz)
12	122.9	5.20 (1H, t, $J = 7.0$ Hz)
13	134.2	-
14	16.0	1.77 (3H, s)
15	39.7	1.96 (2H, m)
16	26.6	2.05 (2H, m)
17	124.5	5.08 (1H, t, $J = 7.0$ Hz)
18	131.0	-
19	17.5	1.58 (3H, s)
20	25.5	1.65 (3H, s)
21	27.6	2.82 (1H, brs)
22	45.9	2.20 (1H, m)
23	21.9	1.32, 0.90 (each 1H, m)
24	37.4	1.82, 1.47 (each 1H, m)
25	75.9	-
26	34.8	2.18 (1H, ddd, $J = 13.2, 4.4, 3.0$ Hz) 1.86 (1H, dd, $J = 13.2, 1.5$ Hz)
27	28.7	1.43 (3H, s)
28	84.5	-
29	29.6	1.55 (3H, s)
30	24.2	1.06 (3H, s)
OH-1	-	14.07 (1H, s)

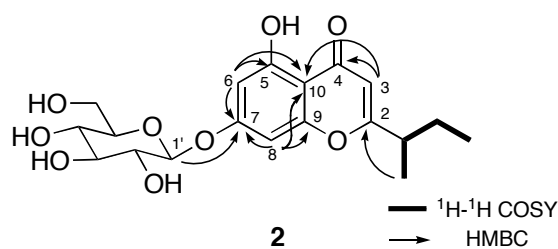
<sup>a</sup>Coupling constants given ( $J$ , Hz) in parentheses.

**Figure 1.** Selected 2D NMR correlations for p etiolin D (**1**)



**Figure 2.** ORTEP drawing of petiolin D (**1**)

Petiolin E (**2**) showed the pseudomolecular ion peak at  $m/z$  431 ( $M+Cl$ )<sup>-</sup> in the ESIMS, and the HRESIMS analysis revealed the molecular formula to be  $C_{19}H_{24}^{35}ClO_9$  [ $m/z$  431.11126 ( $M+^{35}Cl$ )<sup>-</sup>,  $\Delta$  +1.2 mmu]. IR absorptions (1662, 1621, and 1579  $cm^{-1}$ ) suggested the presence of chromone functionality.<sup>12</sup> The <sup>1</sup>H NMR spectrum showed signals of a pair of *meta*-coupled aromatic protons [ $\delta_H$  6.69 and 6.48 (each 1H, d,  $J$  = 1.8 Hz)], an olefin proton [ $\delta_H$  6.11 (1H, s)], an isobutyl group [ $\delta_H$  2.67 (1H, tq,  $J$  = 7.0, 7.0 Hz), 1.76 and 1.64 (each 1H, dq,  $J$  = 7.0, 7.0 Hz), 1.30 and 0.94 (each 3H, d,  $J$  = 7.0 Hz)], and an anomeric proton [ $\delta_H$  5.03 (1H, d,  $J$  = 6.9 Hz)]. The <sup>13</sup>C NMR spectrum exhibited signals due to a conjugated carbonyl carbon, six aromatic carbons, a trisubstituted olefin, an isobutyl group, and a sugar moiety (Table 2). From these data, **2** was elucidated to be a isobutylchromone glycoside. The aglycone of **2** was deduced to be 5,7-dihydroxy-2-isobutylchromone from the analysis of the <sup>1</sup>H-<sup>1</sup>H COSY and HMBC spectra (Figure 3). <sup>13</sup>C NMR chemical shifts of the sugar moiety in **2** were coincident with those of quercetin-3-*O*- $\beta$ -D-glucoside.<sup>13</sup> The HMBC correlation of H-1' to C-7 indicated that the glucosyl moiety was connected to a hydroxyl group at C-7, and its  $\beta$ -glycoside linkage was derived from the  $J$ -value (6.9 Hz) of the anomeric proton signal.



**Figure 3.** Selected 2D NMR correlations for petiolin E (**2**)

**Table 2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data for Petiolin E (**2**) in  $\text{CD}_3\text{OD}$ .

position	$^{13}\text{C}$	$^1\text{H}^a$
2	176.3	-
3	106.9	6.11 (1H, s)
4	184.1	-
5	162.8	-
6	100.9	6.48 (1H, d, $J = 1.8$ Hz)
7	164.6	-
8	95.7	6.69 (1H, d, $J = 1.8$ Hz)
9	159.3	-
10	107.8	-
1'	101.4	5.03 (1H, d, $J = 6.9$ Hz)
2'	74.5	3.30 - 3.51 (1H, m)
3'	77.6	3.30 - 3.51 (1H, m)
4'	71.0	3.30 - 3.51 (1H, m)
5'	78.1	3.30 - 3.51 (1H, m)
6'	62.2	3.90 (1H, brd, $J = 12.0$ Hz) 3.70 (1H, dd, $J = 12.0, 5.6$ Hz)
2-iBu	41.6	2.67 (1H, tq, $J = 7.0, 7.0$ Hz)
	28.4	1.76, 1.64 (each 1H, dq, $J = 7.0, 7.0$ Hz)
	18.0	1.30 (3H, d, $J = 7.0$ Hz)
	11.7	0.94 (3H, t, $J = 7.0$ Hz)

<sup>a</sup>Coupling constants given ( $J$ , Hz) in parentheses.

The sugar moiety was assigned as  $\text{D}$ -glucopyranose by chiral HPLC analysis of  $O$ -benzoyl derivatives of the methanolysis products of **2**.<sup>14</sup> Thus, the structure of **2** was elucidated to be 5,7-dihydroxy-2-isobutylchromone-7- $O$ - $\beta$ - $\text{D}$ -glucopyranoside.

Petiolin D (**1**) is a new phloroglucinol derivative consisting of a citran skeleton, a geranyl group, and a 2-methylpropanoyl group, while petiolin E (**2**) is a new chromone-7- $O$ - $\beta$ - $\text{D}$ -glucopyranoside having an isobutyl group at C-2. Though various phloroglucinol derivatives consisted of a citran skeleton were found in natural sources,<sup>15,16</sup> a derivative having a citran skeleton with a geranyl group attached to its benzene ring like petiolin D (**1**) has not been reported so far. Petiolins D (**1**) and E (**2**) showed no cytotoxicity against murine lymphoma L1210 cells and human epidermoid carcinoma KB cells (both  $\text{IC}_{50} > 10$   $\mu\text{g/mL}$ ), while **1** and **2** exhibited a weak antifungal activity against *Aspergillus niger* (both MIC, 33.3  $\mu\text{g/mL}$ ).

## EXPERIMENTAL

### General Experimental Procedures

Optical rotations were recorded on a JASCO P-1030 digital polarimeter. IR and UV spectra were recorded on JASCO FT/IR-230 and Shimadzu UV-1600PC spectrophotometers, respectively. NMR spectra were measured by a JEOL ECA 500 spectrometer. The 7.27 and 76.9 ppm resonances of residual

CHCl<sub>3</sub> were used as internal references for <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively. ESIMS spectra were recorded on a JEOL JMS-T100LP.

### Plant Material

*Hypericum pseudopetiolum* var. *kiusianum* was collected in Kochi Prefecture, Japan in August 2005. Herbarium specimens were deposited in the botanical garden of the University of Tokushima (specimen number: UTP98013).

### Extraction and Isolation

The aerial parts of *H. pseudopetiolum* var. *kiusianum* (320 g) were extracted with MeOH (3L x 3), and the extracts were partitioned successively with *n*-hexane (300 mL x 3), EtOAc (300 mL x 3), and H<sub>2</sub>O (300 mL). The *n*-hexane-soluble portions were subjected to a silica gel column (*n*-hexane / EtOAc), a Sephadex LH-20 column (EtOH), a C<sub>18</sub> column (MeOH/H<sub>2</sub>O, 85: 15) chromatographies, and then C<sub>18</sub> reversed-phase HPLC (Mightysil RP-18, Kanto Chemical Co., Ltd, 10 x 250 mm; flow rate 3.0 mL/min; UV detection at 254 nm; eluent MeOH/H<sub>2</sub>O, 95:5) to afford petiolin D (**1**, 2.5 mg, 0.0008%). The EtOAc-soluble portions were applied to a Sephadex LH-20 column (H<sub>2</sub>O → MeOH), a C<sub>18</sub> column (MeOH/H<sub>2</sub>O), a silica gel column (CHCl<sub>3</sub>/MeOH), and then C<sub>18</sub> reversed-phase HPLC (Mighty sil RP-18, Kanto Chemical Co. Ltd, 10 x 250 mm; flow rate 3.0 mL/min; UV detection at 254 nm; eluent MeOH/H<sub>2</sub>O, 1:1, 0.1 % TFA) to give petiolin E (**2**, 2.4 mg, 0.0008%).

**Petiolin D (1)**: Colorless crystal; mp 110 – 112 °C; UV (MeOH) λ<sub>max</sub> 240 (ε 15100), 299 (14200), 364 (2470) nm; IR (KBr) ν<sub>max</sub> 3411 and 1613 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR data (Table 1); ESIMS *m/z* 489 (M+Na)<sup>+</sup>; HRESIMS: *m/z* 489.2973 (M+Na)<sup>+</sup> (calcd for C<sub>30</sub>H<sub>42</sub>O<sub>4</sub>Na, 489.2981).

**Petiolin E (2)**: Colorless amorphous; [α]<sub>D</sub><sup>23</sup> -34.4 (*c* 0.48 MeOH); UV (MeOH) λ<sub>max</sub> 257 (ε 9200), 286 (3695), and 320 (2175) nm; IR (KBr) ν<sub>max</sub> 3408, 1662, 1621, and 1579 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR data (Table 2); ESIMS *m/z* 431 (M+<sup>35</sup>Cl)<sup>-</sup>; HRESIMS: *m/z* 431.1113 (M+<sup>35</sup>Cl)<sup>-</sup> (calcd for C<sub>19</sub>H<sub>24</sub><sup>35</sup>ClO<sub>9</sub>, 431.1101).

### X-Ray Analysis of Petiolin D (1)

Petiolin D (**1**) was crystallized as colorless platelets from MeOH/water. The crystal having approximate dimensions of 0.20x0.20x0.02 mm was mounted in a loop. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-Kα radiation (1.54187Å) at -180°C. Crystal data: Formula C<sub>30</sub>H<sub>42</sub>O<sub>4</sub>, Formula weight 466.66, Space group *P*-1(#2), *a*=9.56002(17)Å,

$b=9.74718(18)$ ,  $c=28.0157(5)$ ,  $\alpha=88.8543(7)^\circ$ ,  $\beta=86.5058(7)$ ,  $\gamma=85.7846(7)$ ,  $V=2598.38(8)\text{\AA}^3$ ,  $Z=4$ ,  $D_{\text{calcd}}=1.193\text{ g/cm}^3$ , 39766 reflections measured, 9338 reflections unique,  $2\theta_{\text{max}}=136.5^\circ$ ,  $R_{\text{int}}=0.062$ ,  $R_I=\Sigma ||Fo|-|Fc|| / \Sigma |Fo| = 0.0572$  for 6648 reflections with  $I>2\sigma(I)$ ,  $wR_2=[\Sigma (w(Fo^2-Fc^2))^2 / \Sigma w(Fo^2)^2]^{1/2} = 0.1581$  for all reflections, goodness of fit 1.043. The structure was solved by direct methods (SIR2002)<sup>17</sup> and expanded using Fourier techniques.<sup>18</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using CrystalStructure<sup>19</sup> except for refinement, which was performed using SHELXL-97.<sup>20</sup> Crystallographic data for petiolin D (**1**) have been deposited at the Cambridge Crystallographic Data Center (deposition number CCDC 692371).

### Stereochemical Assignment of the Sugar Moiety in Petiolin E (**2**).

Petiolin E (**2**, 0.3 mg) was treated with 3% HCl/MeOH (300  $\mu\text{L}$ ) at 110  $^\circ\text{C}$  for 1 h. After the solvent was removed by nitrogen stream, to the residue was added EtOAc (100  $\mu\text{L}$ ), and the EtOAc solution was extracted with H<sub>2</sub>O (100  $\mu\text{L}$  x 3). The aqueous fraction evaporated in vacuo was treated pyridine (100  $\mu\text{L}$ ), triethylamine (15  $\mu\text{L}$ ), and benzoyl chloride (15  $\mu\text{L}$ ), at rt for 21 h. After addition of MeOH (100  $\mu\text{L}$ ), the reaction mixture was extracted with *n*-hexane (100  $\mu\text{L}$  x 3). The *n*-hexane-soluble fraction was evaporated in vacuo to afford *O*-benzoyl/methyl derivative of the sugar units of **2**. Authentic D- and L-glucose were treated with benzoyl chloride as described above to afford *O*-benzoyl/methyl derivatives of D- and L-glucose, respectively. The *O*-benzoyl/methyl derivatives were subjected to chiral HPLC analyses using Chiralpak OP(+) (Daicel Chemical Industry, Ltd., 4.6 x 250 mm; MeOH; flow rate 0.5 mL/min; UV detection at 254 nm). The retention time of *O*-benzoyl/methyl derivative of methanolysis product of **2** was found to be 13.7 min, while the retention times of *O*-benzoyl/methyl derivatives of authentic D- and L-glucose were found to be 13.7 and 14.5 min, respectively.

### ACKNOWLEDGMENTS

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