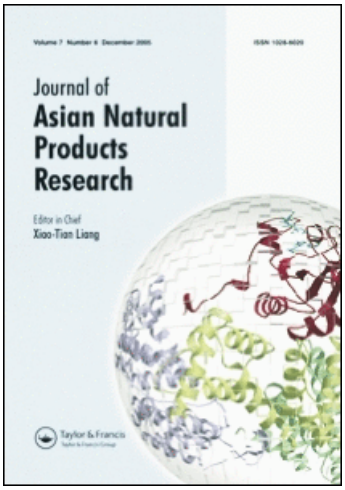

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A new lignan glycoside from the rhizomes of *Imperata cylindrica*

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A new lignan glycoside, 6-acetyl-1-[1,3-(4,4′-dihydroxy-3,3′-dimethoxy-β-truxinyl)-β-D-fructofuranosyl]-α-D-glucopyranoside (**1**), named impecyloside, was isolated from the rhizomes of *Imperata cylindrica*. The structure of the compound was determined by spectroscopic data including FABMS, UV, IR, ^{1}H NMR and ^{13}C NMR (DEPT) and 2D NMR (COSY, HSQC, HMBC).

Keywords: *Imperata cylindrica*; Impecyloside; Gramineae; Lignan glycoside

1. Introduction

Imperata cylindrica (Gramineae) is an aggressive, rhizomatous, perennial grass widely distributed in East Asia. The rhizomes of this plant have traditionally been used as a diuretic, an anti-inflammatory and an antipyretic agent in Korean herbal medicine.[1] Also, neuroprotective compounds from MeOH-extract have been reported.[2] Previous phytochemical studies on the rhizomes of *I. cylindrica* have resulted in the isolation of various compounds such as arundoin, cylindrin, cylindol, cylindrene, graminone and siderin.[3–6] This paper describes the isolation and identification of a new β-truxinic acid derivative with an acetylated sucrose moiety from the rhizomes of *I. cylindrica*.

2. Results and discussion

A new β-truxinic acid derivative was isolated as a yellow amorphous powder from methanol, exhibiting an UV absorption maximum at 212 nm. The compound was freely soluble in water and in methanol. The molecular formula, $C_{34}H_{40}O_{18}$, was deduced from negative HRFAB–MS at *m/z* 735.2139 $[M-H]^-$. The IR absorption bands at 3400, 2937, 1730, 1600 cm^{-1} were due to hydroxyl, alkane, ester carbonyl and aromatic functions. In the ^{1}H NMR spectrum, two methoxy proton signals were observed at δ 3.61 and 3.73, along with six aromatic protons [δ 6.76 (br s, H-2), 7.03 (d, J = 8.0 Hz, H-5), 6.94 (br d, J = 8.0 Hz, H-6), 6.88 (br s, H-2′), 6.97 (d, J = 8.0 Hz, H-5′), 6.71 (br d, J = 8.0 Hz, H-6′)] suggesting the presence of a dual 1,3,4-trisubstituted phenyl moiety. There were some oxygenated methine and methylene signals of carbohydrate moieties in the region from δ 4.22 to 6.18 including one anomeric proton doublet at δ 6.18 with a coupling constant (J) of 3.2 Hz, an indicating α-glucosyl form.[7] In the aliphatic region, methine proton signals at δ 4.80 (H-7′), 4.57 (H-7), 4.49 (H-8), and 4.37 (H-8′) from the cyclobutane ring and acetyl-CH_3 proton signal at δ 1.88 were observed. The ^{13}C NMR spectrum indicated thirty-four carbon signals. The multiplicity of each carbon was determined using DEPT experiment. In the low field region, three carbonyl signals at δ 171.1 (C-1′′′′), 171.9 (C-9′) and 174.5 (C-9) were observed. In the aromatic region, six methine carbons [δ 112.7 (C-2, 2′), 115.9 (C-5′), 116.1 (C-5), 121.1 (C-6′), 121.5 (C-6)], two quaternary carbons [δ 130.3 (C-1′), 130.5 (C-1)] and four oxygenated quaternary carbon [δ 146.6 (C-4′), 146.7 (C-4), 148.1 (C-3′), 148.3 (C-3)] signals due to the dual 1,3,4-trisubstituted phenyl moiety structure were observed. Twelve oxygenated carbon signals of a carbohydrate moiety were observed from δ 63.3 to 109.6 including two anomeric carbon signals at δ 94.2 (C-1′′′) and 109.6 (C-2′′) whose chemical shifts indicated the carbohydrate to be composed of a glucopyranose with some acetylated portion and a fructopyranose. In the aliphatic region, four methine carbon signals at δ 43.9 (C-8), 44.5 (C-8′), 44.8 (C-7′) and 45.8 (C-7) of a cyclobutane ring, and an acetyl-CH_3 carbon signal at δ 20.7 (C-2′′′′) were observed. In the HMBC spectrum, the anomeric proton signal of glucopyranosyl moiety at δ 6.18 showed correlations with an oxygenated carbon signal of the fructopyranosyl moiety at δ 109.6 (C-2′′), indicating the oligosaccharide to be a sucrose [β-D-fructofuranosyl-(2 → 1)-α-D-glucopyranose]. Two carbonyl carbon

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signals at δ 174.5 (C-9) and 171.9 (C-9′) showed correlations with oxygenated methine proton signals of the fructopyranosyl moiety at δ 5.26 (H-1″) and 5.68 (H-3″), respectively. These results suggested ester bond formation at C-1″ and C-3″, confirmed by downfield shifts of the two proton signals owing to the esterification effect, as H-1″ and H-3″ signals of D-fructopyranose were usually observed at ca δ 3.60 and 4.10, respectively.[8,9] Another acetyl carbonyl carbon signal at δ 171.1 (C-1‴′) showed a cross peak with an oxygenated methylene proton signal at δ 4.93 of the glucopyranosyl moiety (H-6‴), meaning the hydroxy of C-6‴ was acetylated, also confirmed by the downfield shift of the proton signal; typically observed at ca δ 3.70 to 3.80.[8,9] The large coupling constants ($J_{7,7'} = 9.6$ and $J_{8,8'} = 11.2$ Hz) of methine protons of the cyclobutane ring resulted in *cis* configuration for pair H-7/H-7′ and H-8/H-8′. Also, the coupling constants ($J_{7,8} = 5.2$ and $J_{7',8'} = 5.2$ Hz) of the methine protons led to inference of *trans* configuration for the H-7/H-8 and H-7′/H-8′ pairs.[9] Therefore, the structure of compound **1** (Figure 1) was determined to be 6-acetyl-1-[1,3-(4,4′-dihydroxy-3,3′-dimethoxy-β-truxinyl)-β-D-fructofuranosyl]-α-D-glucopyranoside, named impecyloside.

The aglycone moiety of this glycoside, β-truxinic acid, and its sucrosyl glycoside have been isolated from tougucao (*Incarvillea sinensis*) and oats, respectively.[10,11] However, no β-truxinic acid derivatives have been reported from *Imperata cylindrica*. Also, organic solvents causing the acetylation reaction during extraction, fractionation and column chromatography procedure were not used, so impecyloside must be a natural compound, rather than artificial. The very high anti-inflammatory activities of β-truxinic acid and its derivative compounds have been previously reported.[11]

3. Experimental

3.1 General experimental procedures

Optical rotation was recorded on a JASCO P-1010 digital polarimeter (Tokyo, Japan). UV spectra were measured on a Shimadzu UV-1601 (Kyoto, Japan). The IR spectrum was obtained with a Perkin Elmer Spectrum One FT-IR spectrometer, CaF_2 window in MeOH (Buckinghamshire, UK). FAB–MS data were recorded on a JEOL JMS-700 (Tokyo, Japan). ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and 2D NMR spectra were recorded on a Varian Unity Inova AS-400 FT-NMR spectrometer (California, USA). Pyridine-d_5 with TMS as internal standard was purchased from Sigma (St. Louis, MO, USA).

3.2 Plant material

The rhizomes of *Imperata cylindrica* were purchased at Kyungdongmart, a herbal drug store in Seoul, Korea and identified by Professor Dae-Keun Kim, College of Pharmacy, Woosuk University, Jeonju, Korea. A voucher specimen (KHU050731) is reserved at the Laboratory of Natural Products Chemistry, Kyung Hee University, Suwon, Korea.

3.3 Extration and isolation

Dried rhizomes of *I. cylindrica* (1.5 kg) were extracted with 80% aqueous MeOH (2 L × 3) at room temperature. The extracts were partitioned with water (1 L), EtOAc (1 L × 3) and *n*-BuOH (0.8 L × 3), successively. The concentrated *n*-BuOH extract (20 g) was applied to a Diaion-HP20 column (12 × 60 cm) with a gradient eluting of H_2O/MeOH (1:0 → 0:1) and the obtained fractions were checked by TLC. The 80% MeOH fraction [2 g, V_e/V_t (elution volume/total volume) 0.70–0.80] was

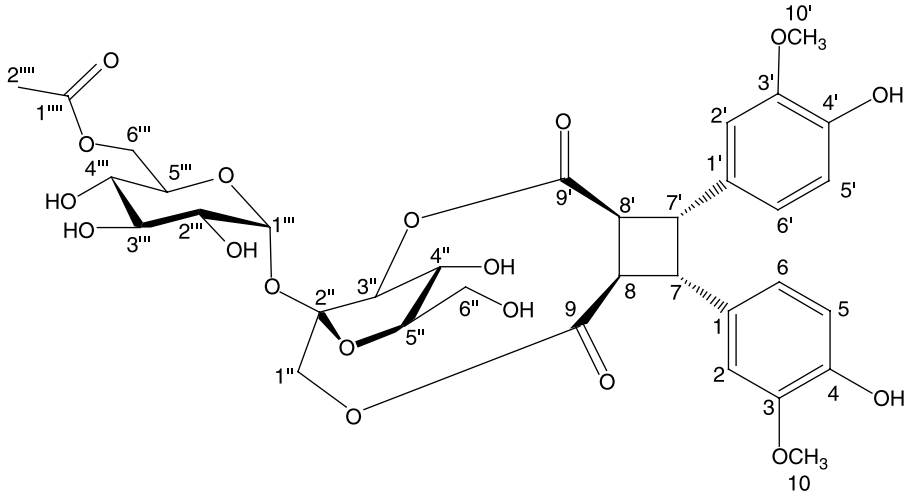

Figure 1. Chemical structure of compound **1**.

Table 1. ^{1}H NMR and ^{13}C NMR spectral data, and HMBC correlations of compound **1** in pyridine-d_5.

	Aglycone moiety				Sucrose moiety		
No.	δ_C (multiplicity)	δ_H (coupling pattern, J in Hz)	HMBC (*H* to *C*)	No.	δ_C (multiplicity)	δ_H (coupling pattern, *J* in Hz)	HMBC (*H* to *C*)
1	130.5 (C)	–		1‴	94.2 (CH)	6.18 (d, 3.2)	C-2‴, C-3‴, C-2‴
2	112.7 (CH)	6.76 (br s)	C-1, C-3	2‴	73.5 (CH)	4.22 (dd, 3.2, 8.8)	C-3‴, C-4‴
3	148.3 (C)	–		3‴	75.4 (CH)	4.78 (dd, 8.8, 8.4)	C-2‴, C-4‴
4	146.7 (C)	–		4‴	71.9 (CH)	4.28 (dd, 8.4, 8.8)	C-3‴, C-5‴
5	116.1 (CH)	7.03 (d, 8.0)	C-4, C-6	5‴	71.3 (CH)	5.24 (ddd, 8.8, 3.2, 4.4)	C-3‴, C-4‴, C-6‴
6	121.5 (CH)	6.94 (br d, 8.0)	C-5, C-1	6‴	64.8 (CH_2)	4.93 (dd, 4.4, 12.0) 5.26 (dd, 3.2, 12.0)	C-5‴, C-1⁗
7	45.8 (CH)	4.57 (dd, 5.2, 9.6)	C-1, C-8, C-7′	1″	65.0 (CH_2)	5.26 (d, 12.0) 4.33 (d, 12.0)	C-4″, C-9
8	43.9 (CH)	4.49 (dd, 5.2, 11.2)	C-7, C-8′, C-9	2″	109.6 (C)	–	
9	174.5 (C)	–		3″	79.7 (CH)	5.68 (s)	C-2″, C-4″, C-5″, C-9′
10	55.8 (CH_3)	3.73 (3H, s)	C-3	4″	88.8 (CH)	4.66 (br s)	C-2″,C-3″, C-5″, C-1″
1′	130.3 (C)	–		5″	75.0 (CH)	5.13 (dd, 3.8, 5.6)	C-2″, C-4″, C-6″
2′	112.7 (CH)	6.88 (br s)	C-1′, C-3′	6″	63.3 (CH_2)	4.47 (dd, 3.8, 12.4) 4.50 (dd, 4.4, 12.4)	C-4″, C-5″
3′	148.1 (C)	–		1⁗	171.1 (C)	–	
4′	146.6 (C)	–		2⁗	20.7 (CH_3)	1.88 (3H, s)	C-1⁗
5′	115.9 (CH)	6.97 (d, 8.0)	C-4′, C-6′				
6′	121.1 (CH)	6.71 (br d, 8.0)	C-5′, C-1′				
7′	44.8 (CH)	4.80 (dd, 5.2, 9.6)	C-7, C-8′, C-1′				
8′	44.5 (CH)	4.37 (dd, 5.2, 11.2)	C-7′, C-8, C-9′				
9′	171.9 (C)	–					
10′	55.7 (CH_3)	3.61 (3H, s)	C-3′				

applied to a silica gel (Merck) column (10 × 60 cm) chromatography and eluted with $CHCl_3$/MeOH/H_2O (10:3:1) resulting in six fractions monitored by TLC. Fraction 3 (250 mg, V_e/V_t 0.45–0.60) was applied to an ODS (Merck) column (2.5 × 30 cm) chromatography eluted with MeOH/H_2O (3:1), yielding compound **1** [33 mg, V_e/V_t 0.53–0.60, TLC (RP-18 F_{254}) R_f 0.55 in MeOH/H_2O = 5:1].

*3.3.1 Impecyloside (**1**)*

Yellow amorphous powder (MeOH); $[\alpha]_D^{25}$ + 12 (*c* 0.01, MeOH); IR ν_{max} (CaF_2 window in MeOH) cm^{-1}: 3400, 2937, 1730, 1600, 1453, 1430, 1365; UV λ_{max} (MeOH): 212 nm; FAB–MS (negative) *m/z*: 735 $[M - H]^-$, 693, 559, 453, 421, 405, 271, 183, 175, 133; HRFAB–MS (negative) *m/z*: 735.2139 $[M - H]^-$ (calcd. for $C_{34}H_{39}O_{18}$, 735.2136); NMR spectral data: see Table 1.

Acknowledgements

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References

[1] J.H. Park, *Medicinal Plants of Korea* (Shinil Publishing Co., Seoul, 2004), p. 101.
[2] J.S. Yoon, M.K. Lee, S.H. Sung, and Y.C. Kim, *J. Nat. Prod.* **69**, 290 (2006).
[3] K. Nishimoto, M. Ito, and S. Natori, *Tetrahedron* **24**, 725 (1968).
[4] K. Matsunaga, M. Ikeda, M. Shibuya, and Y. Ohizuni, *J. Nat. Prod.* **57**, 1290 (1994).
[5] K. Matsunaga, M. Shibuya, and Y. Ohizuni, *J. Nat. Prod.* **57**, 1183 (1994).
[6] M. Wang, S. Wang, Q. Sun, and L. Wu, *J. Chin. Pharm. Sci.* **5**, 53 (1996).
[7] G. Descotes, G. Muller, and J. Mentech, *Carbohydr. Res.* **134**, 313–323(1984).
[8] Y.G. Goyda, A.F. Abdel-Baky, K.M. Mohamed, F.M. Darwish, R. Kasai, and K. Yamasaki, *Nat. Prod. Res.* **20**, 935 (2006).
[9] C. Ceorgopoulou, N. Aligiannis, N. Fokialakis, S. Mitaku, and J. Asian, *Nat. Prod. Res.* **7**, 799 (2005).
[10] L.H. Dimberg, R.E. Andersson, S. Gohil, S. Bryngelsson, and L.N. Lundgren, *Phytochemistry* **56**, 843 (2001).
[11] Y.M. Chi, M. Nakamura, X.Y. Zhao, T. Yoshizawa, W.M. Yan, F. Hashimoto, J. Kinzo, T. Nohara, and S. Sakurada, *Biol. Pharm. Bull.* **29**, 580 (2006).