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PHENOLIC COMPOUNDS FROM THE ROOT OF *Phragmites communis*

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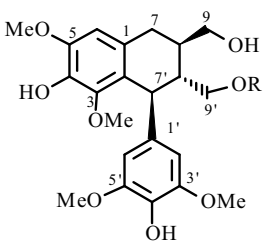
Phragmitis Rhizoma (*Phragmitis communis*), rhizome of reed, has been used as an oriental traditional medicine for esophageal cancer, vomiting, lung abscess, fever, dysurea, and tetrodotoxin detoxication [1]. Previously, β-sitosterol, vanillic acid, ferulic acid, *p*-hydroxybenzaldehyde, and *p*-cinnamic acid were isolated from Phragmitis Rhizoma and their anti-hyperlipidemic effect reported [2]. Serotonin, tryptophan, and tryptamine were identified by co-chromatography with the respective authentic compounds from Phragmitis Rhizoma [3].

In the present study, a known phenolic acid and two lignans were isolated from Phragmitis Rhizoma for the first time.

The fresh root of *P. communis* was extracted with aqueous acetone, and the extract was subjected to a combination of Sephadex LH-20, MCI gel, and YMC-ODS column chromatography to afford methyl gallate (**1**), (+)-lyoniresinol (**2**), and (+)-lyoniresinol-3α-*O*-β-D-glucopyranoside (**3**).

Compound **1** gave a brown coloration when sprayed with alcoholic ferric chloride on TLC. Negative LC MS spectrum of **1** showed a molecular ion peak at *m/z* 182.8 $[M–H]^–$, and the ^{1}H NMR spectrum of **1** showed two singlet at δ 7.05 (2H, H-2,6) and δ 3.81 (OCH_3) attributable to a galloyl and a methoxyl proton, respectively. The ^{13}C NMR spectrum of **1** also showed a galloyl group at δ 110.1 (C-2 and 6), 139.9 (C-4), 146.7 (C-3 and 5), and 169.3 (COO) and a methoxyl group at δ 52.3. These results suggested that **1** is methyl gallate, which was confirmed by comparisons with the spectral data in the literature [4].

Compounds **2** and **3** gave a green coloration when heated after spraying with 10% H_2SO_4 and showed a dark brown coloration when sprayed with alcoholic ferric chloride on TLC. The negative LC MS spectrum of **2** and **3** showed a molecular ion peak at *m/z* 417.6 $[M–H]^–$ and 581.4 $[M–H]^–$. The ^{1}H NMR spectrum of **2** showed three singlet signals at δ 3.69, 3.33, and 3.80 corresponding to the signals from four methoxyl groups. The ^{1}H NMR spectrum of **2** also showed two singlet signals attributable to a galloyl and an aromatic methine proton at δ 6.40 (H-2′, 6′) and 6.55 (H-6), two alcoholic methylene signals at δ 3.49 (H-9′), 3.52 (H-9a), and 3.59 (H-9b), three methine signals at δ 4.26 (H-7′), 1.95 (H-8′) and 1.59 (H-8), and another methylene signal at 2.65 (H-7eq) and 2.55 (H-7ax). The ^{13}C NMR spectrum of **2** showed four methoxyl groups at δ 55.5, 55.9 (2C), and 58.8, a methylene and two alcoholic methylenes at δ 32.8, 65.5, and 62.8, and three methines at δ 41.5, 38.8, and 48.2 which indicated an estimated two sinapyl alcohols of the cyclolignan type (Table 1). Each proton and carbon assignment could be completed by ^{1}H–^{1}H COSY, HSQC, and HMBC in the form of two cyclolignan sinapyl alcohol as 4,4′,9,9′-tetrahydroxy-3,3′,5,5′-tetramethoxy-2,7′-cyclolignan[(+)-lyoniresinol] [5].



2, 3

2: R = H; **3:** R = Glc

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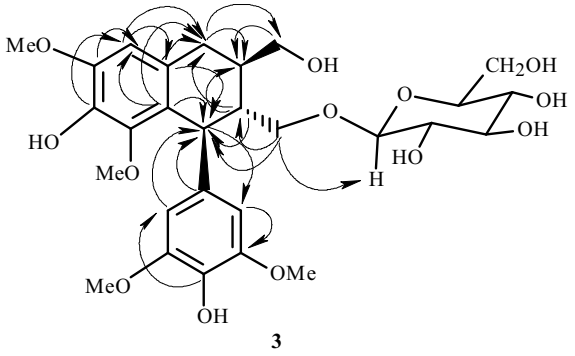
TABLE 1. ^{13}C NMR Spectra of Compounds **2** and **3**

C atom	**2**	**2a**	**3**	**3a**
1	129.0	128.8	129.7	130.2
2	125.5	125.1	126.1	126.4
3	146.2	146.6	146.8	147.6
4	137.7	137.3	138.3	138.9
5	146.9	147.0	147.7	148.6
6	106.4	107.0	107.3	107.8
7	32.8	32.3	33.5	33.8
8	38.8	39.3	40.0	40.6
9	65.5	64.9	65.4	66.2
1′	138.3	137.8	138.9	139.3
2′	106.3	106.5	106.7	106.9
3′	147.5	147.7	148.2	149.0
4′	133.8	134.	134.2	134.5
5′	147.5	147.7	148.2	149.0
6′	106.3	106.5	106.7	106.9
7′	41.5	40.4	42.3	42.8
8′	48.2	46.8	46.1	46.7
9′	62.8	62.7	70.8	71.5
Glc-1			104.1	104.8
Glc-2			74.4	75.1
Glc-3			77.4	78.2
Glc-4			71.0	71.7
Glc-5			77.2	77.9
Glc-6			62.2	62.8
3-OCH_3	58.8	59.2	59.6	60.2
5-OCH_3	55.5	55.9	56.3	56.6
3′-OCH_3	55.9	56.4	56.7	56.9
5′-OCH_3	55.9	56.4	56.7	56.9

2a: (+)-Lyoniresinol, **3a**: (+)-lyoniresinol-3α-*O*-(*β*-D-glucopyranosyl) [5, 6].



3

Fig. 1. HMBC correlation of compound **3**.

The ^1H and ^{13}C NMR spectra of **3** showed one glucopyranosyl moiety at δ 4.31 (1H, d, J = 7.5 Hz, Glc-1), 3.79–3.59 (1H, m, Glc-6), 3.43 (1H, m, Glc-3), 3.31 (1H, m, Glc-4), 3.21 (1H, m, Glc-2), and at δ 104.1 (Glc-1), 77.4 (Glc-3), 77.2 (Glc-5), 77.4 (Glc-2), 71.0 (Glc-4), and 62.2 (Glc-6). Except for these signals, these spectra were almost coincident with **2**. These data indicated that **3** is the monoglucopyranoside of **2**. Each proton and carbon assignment was completed by ^1H–^1H COSY, and HSQC experiments, and the correlation between C-9′ and the glucose anomeric proton in the HMBC spectrum of **3** showed that the linkage of sugar is C-9′ (Fig. 1). From these results, **3** was identified as (+)-lyoniresinol-3*α*-*O*-*β*-D-glucopyranoside [6, 7]. Noteworthy is the fact that compounds **1–3** were isolated for the first time from the Phragmitis Rhizoma.

General Experimental Procedures. MS were obtained on a Varian Saturn 4D mass spectrometer (Varian, Inc., U.S.A.) and JEOL JMS HX-110/110A tandem mass spectrometer (JEOL Ltd., Japan). TLC was carried out on Merck silica gel F_{254}-precoated glass plates and RP-18 F_{254s} plates.

Plant Material. *Phragmitis communis* (Phragmitis Rhizoma) was collected from Wansan Dong, Yungchun City, Kyungbuk, South Korea in June of 2007. A voucher specimen (2007614) was deposited at the herbarium of the College of Pharmacy, Chung-Ang University.

Extraction and Isolation. Phragmitis Rhizoma (5 kg) was extracted with 80% aqueous acetone (3 × 10 L) for 3 days. After removal of Me_2CO in vacuo, the aqueous solution was filtered. The filtrate was concentrated and then applied to a column of Sephadex LH-20 (450 g, 10 × 70 cm). Elution with H_2O containing an increasing proportion of MeOH afforded five fractions.

Repeated column chromatography of fraction 3, which showed a positive color reaction on $FeCl_3$ solution in TLC test over MCI gel with a gradient solvent system of H_2O–MeOH (100:0→50:50), followed by YMC ODS column chromatography with a gradient solvent system of H_2O–MeOH (100:0→50:50), yielded **1** (20.6 mg). Repeated low- pressure liquid column chromatography on YMC ODS gel (400/230 mesh) (H_2O→50% MeOH, gradient system) and Sephadex LH-20 column chromatography (H_2O→50% MeOH, gradient system) yielded **2** (4.3 mg) and **3** (22.4 mg).

Methyl gallate (1), brown amorphous powder, Negative LC MS: *m/z* 182.8 $[M–H]^–$, ^1H NMR (300 MHz, δ, CD_3OD): 3.81 (3H, s, OCH_3), 7.05 (2H, s, H-2, 6). ^{13}C NMR (75 MHz, δ, MeOD-d_4): 169.3 (C-7), 146.7 (C-3, 5), 139.9 (C-4), 121.6 (C-1′), 110.1 (C-2,6′), 52.3 (OCH_3).

(+)-Lyoniresinol (2), brown amorphous powder, negative LC MS: *m/z* 417.6 $[M–H]^–$, ^1H NMR (600 MHz, δ, Me_2CO-d_6 + D_2O, J/Hz): 1.59 (1H, m, H-8), 1.95 (1H, m, H-8′), 2.55 (1H, dd, J = 12.6, 14.5, H-7ax), 2.65 (1H, dd, J = 4.5, 14.5, H-7eq), 3.33 (3H, s, 3-OCH_3), 3.49 (2H, d, J = 6.0, H-9′), 3.52 (1H, m, H-9), 3.59 (1H, m, H-9), 3.69 (6H, s, 3′,5′-OCH_3), 3.80 (3H, s, 5-OCH_3), 4.26 (1H, d, J = 6.0, H-7′), 6.40 (2H, s, H-2′,6′), 6.55 (1H, s, H-6). ^{13}C NMR (150 MHz, Me_2CO-d_6 + D_2O): see Table 1.

(+)-Lyoniresinol-3*α*-*O*-*β*-D-glucopyranoside (3), brown amorphous powder, negative LC MS: *m/z* 581.4 $[M–H]^–$. ^1H NMR (600 MHz, δ, Me_2CO-d_6 + D_2O, J/Hz): 1.65 (1H, m, H-8), 2.07 (1H, m, H-8′), 2.55 (1H, dd, J = 4.5, 14.5, H-7ax), 2.64 (1H in total, dd, J = 4.2, 14.5, H-7eq), 3.25 (1H, m, Glc-2), 3.27 (3H, s, 3-OCH_3), 3.31 (1H, m, Glc-4), 3.29 and 3.62 (2H in total, m, H-9), 3.43 (1H, m, Glc-3), 3.79–3.59 (1H, m, Glc-6), 3.69 (6H in total, s, 3′,5′-OCH_3), 3.78 (3H, s, 3′-OCH_3), 4.31 (1H, d, J = 7.5, Glc-1), 4.34 (1H, m, H-7′), 6.42 (2H, s, H-2′,6′), 6.54 (1H, s, H-6). ^{13}C NMR (150 MHz, Me_2CO-d_6 + D_2O): see Table 1.

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REFERENCES

1. C. M. Kim, M. K. Shin, D. K. Ahn, and K. S. Lee, *An Unabridged Dictionary of Chinese Herbs*, Jeongdam Publication, 1998, pp. 955–958.
2. J. S. Choi, J. H. Lee, and S. Y. Han, *J. Korean Soc. Food Sci. Nutrition*, **24** (4), 523 (1995).
3. Y. H. Kim, C. Y. Lee, and I. S. Kim, *J. Korean Agric. Chem. Soc.,* **19** (1), 24 (1976).
4. J. Y. Oh, U. Choi, Y. S. Kim, and D. H. Shin, *Korean J. Sci. Technol.,* **35** (4), 726 (2003).
5. Z. Zhang, D. Guo, L. Changling, J. Zheng, K. Koike, Z. Jia, and T. Nikaido, *Phytochemistry*, **51**, 469 (1999).
6. K. Tripetch, S. K. Mohamed, K. Ryoji, Y. Kazuo, P. Chayan, and H. Yoshikazu, *Phytochemistry*, **56**, 369 (2001).
7. A. Hans, B. Monika, and T. Ruben, *Phytochemistry*, **45**, 325 (1997).