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Two New Neolignans from the Aerial Parts of *Rodgersia podophylla*

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Two new neolignans (1, 2) were isolated from the aerial parts of *Rodgersia podophylla*, along with four known neolignans, and their structures were elucidated using spectral experiments and comparison with literature data.

Key words *Rodgersia podophylla*; neolignan; Saxifragaceae; 3-methoxy-4-[(2*S*,3*R*)-3-methyl-7-[(*E*)-1-propenyl-2,3-dihydro-1,4-benzodioxin-2-yl]-1,2-benzenediol; 3-methoxy-4-[(2*S*,3*R*)-3-methyl-7-(1-propynyl)-2,3-dihydro-1,4-benzodioxin-2-yl]-1,2-benzenediol

The rhizomes of *Rodgersia podophylla* A. Gray (Saxifragaceae), which is distributed in China, Japan, and Korea, have been used for the treatment of enteritis and bacillary dysentery and have been reported to exhibit antipyretic, analgesic, and hepatoprotective effects.[1)] Phytochemical studies on this plant resulted in the isolation of bergenin, β-peltoboykinolic acid, sterols, monoterpenes, fatty acids, neolignans, and flavonol glycosides.[1—4)] Two of the isolated neolignans have acetylenic functionality, which appeared attractive in the research on this plant. As a part of our ongoing search for biologically active materials in this plant, chromatographic separation and purification of the aerial parts led to the identification of two new neolignans, along with four known neolignans.

Compound **1** exhibited a molecular ion peak at *m/z* 328.1307, corresponding to the formula $C_{19}H_{20}O_5$ in the HR-EI-MS. The UV maxima at 258 and 302 nm were indicative of a lignan skeleton. Careful inspection of the ^{1}H-NMR spectrum of **1** disclosed that this compound contained a methoxy group, two aromatic rings, and two C_3 units. The *ortho*-coupled protons at δ 6.71 (1H, d, J=8.5 Hz, H-5) and 6.95 (1H, d, J=8.5 Hz, H-6) were assigned to H-5 and H-6, respectively, due to a 1,2,3,4-tetrasubstituted benzene ring.[3,4)] The remaining aromatic signals at δ 6.81 (1H, d, J=8.3 Hz, H-5′), 6.84 (1H, d, J=8.3 Hz, H-6′), and 6.91 (1H, s, H-2′) were designated to the protons on a 1,3,4-trisubstituted benzene ring. Additionally, it was found that one of the two C_3 units consisted of a methyl group at δ 1.07 (3H, d, J=7.4 Hz, H-9) and two oxymethines at δ 4.56 (1H, qd, J=7.4, 2.5 Hz, H-8) and 5.35 (1H, d, J=2.5 Hz, H-7), and that another unit had a methyl group at δ 1.83 (3H, d, J=6.5 Hz, H-9′) and two olefinic protons at δ 6.06 (1H, qd, J=15.8, 6.5 Hz, H-8′) and 6.23 (1H, d, J=15.8 Hz, H-7′). The links between C_3 units and benzene rings were established using the HMBC technique. A doublet at δ 5.35 (H-7) showed ^2J correlation with δ 121.9 (C-1), and ^3J correlations with δ 118.6 (C-6) and 144.9 (C-2), which suggested that a 1,2,3,4-tetrasubstituted benzene ring was connected to the C_3 unit that contained two oxymethines and a methyl group. Another C_3 unit was linked to the 1,3,4-trisbustituted benzene ring, which was supported by the cross peaks between δ 6.23 (H-7′) and 131.7 (C-1′), as well as δ 6.06 (H-8′) and 131.7 (C-1′). The connections of two phenylpropanoids deduced from the signals at δ 4.56 (H-8) and 5.35 (H-7) were correlated with δ 141.7 (C-4′) and 143.0 (C-3′) through three bonds, respectively. These HMBC correlations confirmed that C-7 and C-8

Table 1. The ^{1}H- and ^{13}C-NMR Chemical Shifts of Compounds **1** and **2** in $CDCl_3$

	1		**2**	
	H	C	H	C
1		121.9		121.6
2		144.9		144.9
3		136.2		136.3
4		144.6		144.7
5	6.71 (1H, d, J=8.5)	111.5	6.72 (1H, d, J=7.9)	111.4
6	6.95 (1H, d, J=8.5)	118.6	6.94 (1H, d, J=7.9)	118.5
7	5.35 (1H, d, J=2.5)	72.3	5.35 (1H, d, J=2.4)	72.3
8	4.56 (1H, qd, J=7.4, 2.5)	71.8	4.61 (1H, qd, J=6.6, 2.4)	72.0
9	1.07 (3H, d, J=7.4)	13.3	1.08 (3H, d, J=6.6)	13.3
1′		131.7		117.3
2′	6.91 (1H, s)	114.1	6.98 (1H, d, J=1.4)	120.2
3′		143.0		142.7
4′		141.7		142.0
5′	6.81 (1H, d, J=8.3)	117.3	6.81 (1H, d, J=8.3)	116.7
6′	6.84 (1H, d, J=8.3)	119.4	6.93 (1H, dd, J=8.3, 1.4)	125.2
7′	6.23 (1H, d, J=15.8)	130.2		79.3
8′	6.06 (1H, qd, J=15.8, 6.5)	124.0		84.0
9′	1.83 (3H, d, J=6.5)	18.3	2.02 (3H, s)	4.3
$-OCH_3$	3.85 (3H, s)	61.4	3.85 (3H, s)	61.4

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are connected to C-3′ and C-4′, respectively, through *O*-linkages. The position of a methoxy group at δ 3.85 was at C-2 on the 1,2,3,4-tetrasubstituted benzene ring as identified by the cross peaks between δ 3.85 and 144.9 (C-2). Therefore, compound **1** was assumed to be a skeleton of 7,3′-dioxy-8,4′-neolignan with a 1,2,3,4-tetrasubstituted benzene ring. The relative configurations of C-7 and C-8 were determined to be *cis* based on the *J* value (2.5 Hz) between H-7 and H-8 in the ^{1}H-NMR spectrum. The absolute stereochemistry of the C-7 and C-8 was designated as *S* and *R*, respectively, using CD data, which was in good agreement with the stereochemistry reported in the literature.[3)] On the basis of the above extensive analyses, the structure of compound **1** was established as depicted in Fig. 1.

The molecular formula of compound **2** was assigned to be $C_{19}H_{18}O_5$ based on the peak at *m/z* 326.1145 in the HR-EI-MS. The ^{1}H- and ^{13}C-NMR data of compound **2** were similar to those of compound **1**, except that it lacked olefinic protons. Instead of olefinic functionality in **1**, compound **2** displayed two acetylenic carbon signals at δ 79.3 (C-7′) and 84.0 (C-8′) in the ^{13}C-NMR spectrum.[2)] The CD curve of compound **2**, which was analogous to that of compound **1**, led to the conclusion that the absolute configurations of C-7 and C-8 in **2** were *S* and *R*, respectively. Compounds **3**—**6** were elucidated as shown Fig. 1 by comparing their spectral data with those in the literature.[3,4)]

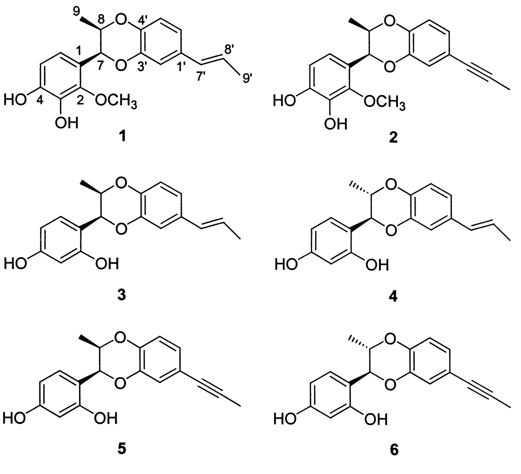

Fig. 1. The Structures of Compounds **1**—**6**

Experimental

General Procedure The optical rotation was measured with a JASCO DIP-1000 digital polarimeter (Tokyo, Japan) and the CD spectra were recorded on a JASCO J-715 spectrometer. HREI-MS spectra were obtained on a JEOL JMS-AX505WA. UV and IR spectra were recorded on a Shimadzu UV-2101 and Perkin Elmer 1710 spectrometer, respectively. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker spectrometer at 400 MHz and 100 MHz, respectively. Column chromatography was performed using Sephadex LH-20 (Pharmacia) and Kiesegel 60 (Art. 7734; Merck, Darmstadt, Germany) column packing materials. TLC was conducted on precoated Kiesegel 60 F_{254} plates (Art. 5715; Merck). Spots on TLC were detected under UV radiation.

Plant Material The aerial parts of *Rodgersia podophylla* A. Gray (Saxifragaceae) were collected from Jinbu, Gangwon province, in 2003. A voucher specimen (SNUPC-011-1) was deposited at Seoul National University.

Extraction and Isolation Dried materials (3.2 kg) were extracted using MeOH, giving a crude extract (300 g). The MeOH extract was successively partitioned with *n*-hexane, CH_2Cl_2, and *n*-BuOH. The *n*-hexane extract (70 g) was subjected to Sephadex LH-20 (400 g) column chromatography using a solvent system (*n*-hexane–CH_2Cl_2–MeOH=10 : 10 : 1), which gave three fractions (RH1, RH2, RH3). The RH2 fraction (1.8 g) was applied to a silica gel (230—400 mesh, Merck, 40 g) column chromatography using an *n*-hexane–EtOAc (10 : 1, 7 : 1, 5 : 1, 3 : 1, 1 : 1, 0 : 1, 900 ml each) gradient that afforded four fractions (RH21, RH22, RH23, RH24). The RH23 fraction (120 mg) was subjected to HPLC [YMC-Pack Ph, MeCN–H_2O 50 : 50 (v/v), 2 ml/min] to provide compounds **1** (1.1 mg, t_R: 32.7 min) and **2** (2.4 mg, t_R: 29.6 min). The RH22 fraction (270 mg), purified by HPLC [YMC J'sphere ODSH80, MeCN–H_2O 50 : 50 (v/v), 2 ml/min], gave compounds **3** (4.5 mg, t_R: 54.7 min), **4** (0.7 mg, t_R: 50.5 min), **5** (1.7 mg, t_R: 38.5 min), and **6** (1.0 mg, t_R: 36.4 min).

Compound **1**: ^{1}H- and ^{13}C-NMR data, see Table 1. IR ν_{max} (KBr) cm^{-1}: 3333, 1583, 1504, 1267. UV λ_{max} (MeOH) nm (log ε): 258 (4.04), 302 (3.62). CD (c=0.08 mg/ml, MeOH) $[\theta]_{212.5}$ −11272, $[\theta]_{232.0}$ 0 $[\theta]_{240.0}$ +4569, $[\theta]_{249.5}$ +2979, $[\theta]_{259.5}$ +3999, $[\theta]_{284.5}$ +411, $[\theta]_{305.5}$ +1671. HR-EI-MS *m/z*: 328.1307 (Calcd for $C_{19}H_{20}O_5$, 328.1311). $[\alpha]_D^{20}$ +24.23° (c=0.06, MeOH).

Compound **2**: ^{1}H- and ^{13}C-NMR data, see Table 1. IR ν_{max} (KBr) cm^{-1}: 3413, 1577, 1503, 1265, 1047, 756. UV λ_{max} (MeOH) nm (log ε): 256 (4.03), 295 (3.53). CD (c=0.006 mg/ml, MeOH) $[\theta]_{218.0}$ −5665, $[\theta]_{229.0}$ 0 $[\theta]_{240.5}$ +15979, $[\theta]_{252.0}$ +7205, $[\theta]_{259.5}$ +9681, $[\theta]_{281.0}$ +1235, $[\theta]_{295.5}$ +2785. HR-EI-MS *m/z*: 326.1145 (Calcd for $C_{19}H_{18}O_5$, 326.1154). $[\alpha]_D^{20}$ +48.3° (c=0.08, MeOH).

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