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ELLAGIC ACID DERIVATIVES FROM THE STEM BARK OF *Dipentodon sinicus*

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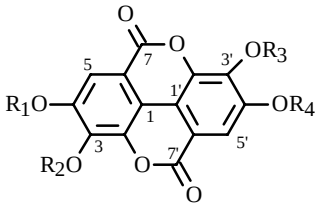
Ellagic acid derivatives were isolated from Dipentodon sinicus *and their structures were identified as 3,3′,4′-tri*-O-*methylellagic acid (**1**), 3,3′-di*-O-*methylellagic acid (**2**), 4,4′-di*-O-*methylellagic acid (**3**), 3,3′-di*-O-*methylellagic acid-4′*-O-α-*L-rhamnopyranoside (**4**), 3,3′,4′-tri*-O-*methylellagic acid-4′*-O-β-*D-glucopyranoside (**5**), 3,3′-di*-O-*methylellagic acid-4′*-O-β-*D-glucopyranoside (**6**), and ellagic acid (**7**). All the compounds were isolated for the first time from the title plant.*

Key words: *Dipentodon sinicus*; ellagic acid derivatives; structure elucidation.

Dipentodon sinicus Dunn is the only member of the genus *Dipentodon* (Family Celastraceae), which has been used as a medicinal plant in the treatment of inflammation and ache by local inhabitants [1]. However, this plant has not been chemically studied. In searching for bioactive substances, we have analyzed the title plant collected from Yunnan, Seven ellagic acid derivatives, 3,3′,4′-tri-*O*-methylellagic acid (**1**), 3,3′-di-*O*-methylellagic acid (**2**), 4,4′-di-*O*-methylellagic acid (**3**), 3,3′-di-*O*-methylellagic acid-4′-*O*-α-L-rhamnopyranoside (**4**), 3,3′,4′-tri-*O*-methylellagic acid-4′-*O*-β-D-glucopyranoside (**5**), 3,3′-di-*O*-methylellagic acid-4′-*O*-β-D-glucopyranoside (**6**), and ellagic acid (**7**) were isolated from the 95% EtOH extracts of this plant.

For the ^{1}H-NMR and ^{13}C-NMR data of compounds **1–7**, see Tables 1 and 2 [2].



1 - 7

1: R_1 = H, R_2 = R_3 = R_4 = Me; **2:** R_1 = R_4 = H, R_2 = R_3 = Me
3: R_1 = R_4 = Me, R_2 = R_3 = H; **4:** R_1 = H, R_2 = R_3 = Me, R_4 = Rha
5: R_1 = R_2 = R_3 = Me, R_4 = Glu; **6:** R_1 = H, R_2 = R_3 = Me, R_4 = Glu
7: R_1 = R_2 = R_3 = R_4 = H

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TABLE 1. ^{1}H NMR Chemical Shifts of Compounds **1-7** (400 MHz, DMSO-d_6, J/Hz)

Atom	**1** [2]	**2** [2]	**3** [3]	**4** [4]	**5** [2]	**6** [2]	**7** [2]
5-H	7.54	7.52	7.49	7.51	7.65	7.51	7.14
5′-H	7.64	7.52	7.49	7.78	7.85	7.81	7.47
3-Me	4.05	4.05	3.98	4.06	4.06	4.05	
3′-Me	4.06	4.05	3.98	4.07	4.11	4.09	
4-Me					4.02		
4′-Me	4.01						
C_1-H of sugar				5.57 (s)	5.17 (d, 7.0)	5.14 (d, 7.5)	

TABLE 2. ^{13}C NMR Chemical Shifts of Compounds **1-7** (100 MHz, DMSO-d_6)

C atom	**1** [2]	**2** [2]	**3** [3]	**4** [4]	**5** [2]	**6** [2]	**7** [2]
1	111.2	111.5	107.3	111.0	111.9	111.9	107.6
2	140.9	141.1	140.9	140.9	141.1	140.9	139.3
3	140.3	140.1	136.2	140.1	140.8	140.5	130.8
4	152.5	152.2	150.1	150.2	151.8	151.3	148.5
5	111.6	111.3	107.0	111.6	112.3	112.0	110.1
6	111.9	112.1	113.4	111.9	112.6	112.8	112.1
7	158.3	158.4	158.8	158.2	158.1	158.5	158.8
1′	112.4	111.5	107.3	114.0	112.8	114.4	107.6
2′	141.5	141.1	140.9	141.5	141.6	141.7	139.3
3′	140.8	140.1	136.2	141.8	140.8	141.8	130.8
4′	153.8	152.2	150.1	152.8	154.2	154.2	148.5
5′	107.5	111.3	107.0	111.7	107.6	112.8	110.1
6′	113.4	112.1	113.4	112.6	113.6	112.9	112.1
7′	158.5	158.4	158.8	158.3	158.3	158.5	158.8
3-OMe	61.0	61.0		60.9	61.2	60.9	
3′-OMe	61.3	61.0		61.5	61.5	61.5	
4-OMe			56.6		56.7		
4′-OMe	56.7		56.6				
1″				99.8	101.2	101.3	
2″				70.4	73.2	73.3	
3″				70.2	77.2	77.2	
4″				71.5	69.4	69.7	
5″				70.0	76.4	76.4	
6″				17.9	60.5	60.5	

EXPERIMENTAL

General. NMR spectra were measured on a Bruker DRX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C spectra) spectrometer. Chemical shifts were expressed in δ values with reference to TMS as internal standard. EI-MS and ESI-MS were carried out on a Finnigan MAT 95 instrument and API2000 LC/MS/MS spectrometer, respectively.

Plant Material. *Dipentodon sinicus* was collected from Xishuang Banna, Yunnan Province, the People's Republic of China and was identified by Prof. Hua Peng of Kunming Institute of Botany, Chinese Academy of Science. A voucher specimen has been deposited in the Herbarium of the Shanghai Institute of Materia Medica.

Extraction and Isolation. The air-dried powdered whole plant of *D. sinicus* (1 kg) was extracted with 95% EtOH (8 L × 3, 2 days each) at room temperature. After removal of solvent in *vacuo*, an extract of 100 g was obtained. The extract

was suspended in H_2O (2 L) and partitioned with petroleum ether (2 L × 5), EtOAc (2 L × 5) and *n*-BuOH (2 L × 5) to give the corresponding fractions A (3 g), B (12 g), and C (28 g).

Fraction B was divided into five subfraction B1~B5 by silica gel column (250 g, 100~200 mesh), using $CHCl_3$–CH_3OH (100:0, 50:1, 25:1, 15:1, 8:1, each 800 ml) as solvents. B1 (1.8 g) was separated over a silica gel column (28 g, 200~300 mesh) with petroleum ether-acetone (6:1) to give **1** (30 mg); Separation of B2 (2.8 g) by a silica gel column (52 g, 200~300 mesh) with petroleum ether–actone (3:1) afforded **2** (30 mg) and **3** (20 mg); B3 (1.5 g) was chromatographed by a silica gel column (35g, 200~300 mesh) eluted with $CHCl_3$–CH_3OH (15:1) to yield **4** (30 mg) and **5** (20 mg); B4 (1.1 g) was chromatographed by a silica gel column (30g, 200~300 mesh) eluted with $CHCl_3$–CH_3OH (12:1) to yield **6** (30 mg); B5 (0.8 g) was chromatographed by a silica gel column (20 g, 200~300 mesh) eluted with $CHCl_3$–CH_3OH (9:1) to yield **7** (30 mg).

3,3′,4′-Tri-*O*-methylellagic acid (1), yellow powder, mp 287~289°C, EI-MS *m/z*: 344 $[M]^+$.

3,3′-Di-*O*-methylellagic acid (2), yellow powder, mp >300°C, EI-MS *m/z*: 330 $[M]^+$.

4,4′-Di-*O*-methylellagic acid (3), yellow powder, mp >300°C, EI-MS *m/z*: 330 $[M]^+$.

3,3′-Di-*O*-methylellagic acid-4′-*O*-α-L-rhamnopyranoside (4), prism crystals, mp 186°C (dec); ESI-MS (negative) *m/z*: 475 $[M-1]^-$.

3,3′,4′-Tri-*O*-methylellagic acid-4′-*O*-β-D-glucopyranoside (5), prism crystals, mp 266~268°C; ESI-MS (negative) *m/z*: 505 $[M-1]^-$.

3,3′-Di-*O*-methylellagic acid-4′-*O*-β-D-glucopyranoside (6), prism crystals, mp 297°C (dec); ESI-MS (negative) *m/z*: 491 $[M-1]^-$.

Ellagic acid (7), yellow powder, mp >300°C, EI-MS *m/z*: 302 $[M]^+$.

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