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NOTE

A New Organic Acid Derived from the Stem of *Alsophila spinulosa* (Hook.) Tryo

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A new organic acid, named 3-acetyl-4-O-β-D-glucopyranoside caffeic acid has been isolated from the Chinese medicinal herb *Alsophila spinulosa* (Hook.) Tryo. The structure was charaterized by ^{1}D and ^{2}D NMR, ^{13}C NMR, ESIMS, HRESIMS spectra.

Key Words: *Alsophila spinulosa*, 3-Acetyl-4-O-β-D-glucopyranosidecaffeic acid, Spectroscopic methods.

Alsophila spinulosa (Hook.) Tryo is known relic plant[1]. Owning to therapeutic effect of the plant on the clinic including arthritic pain, anti-inflammatory, antimicrobial activity *etc.*[2], the stem of *Alsophila spinulosa* has been received a large amount of attentions.

Flavonoids and sitosterols had been reported in the plant's leaves[3]. To our best of knowledge, no details of the chemical constituent of the plant's stem have been reported.

Alsophila spinulosa (Hook.)Tryo was collected in WuTong county of Leshan, Sichuan Province of China in April 2005 and authenticated by Prof. Li-Qun Luo of the Leshan Normal University. A voucher specimen was deposited at Leshan Normal University.

Optical rotations were measured using a Perkin-Elmer model 241 polarimeter. ^{1}D and ^{2}D NMR spectra were measured on a Bruker DRX-400 instrument with TMS as internal standard. Mass spectra were obtained by a VG Auto Spec-3000 spectrometer or on a Finnigan MAT 90 instrument. Column chromatography was performed on silica gel (200-300 mesh; Qingdao Marine Chemical Inc.). Thin-layer chromatography was carried out on silica gel 60 F_{254} on glass plates (Qingdao Marine Chemical Inc.) using various solvent systems.

Extraction and Isolation: Dry herbs of the stem of *Alsophila spinulosa* (Hook.) Tryo (1.0 kg) were extracted with ethanol (3 × 5 L) at room temperature overnight. The extract was suspended in water (800 mL) to form a suspension and then partitioned with EtOAc and *n*-BuOH successively to afford EtOAc extract (36 g) and *n*-BuOH extract (28 g), respectively. The *n*-BuOH extract was chromatographed on a silica gel column employing $CHCl_3$-CH_3OH-H_2O (7:1:0.1 → 2:1:0.1) as eluent to provided compound **1** (16 mg).

3-Acetyl-4-O-β-D-glucopyranosidecaffeic acid (**1**, Fig. 1), amorphous power m.p. 177-178 ºC. $[\alpha]_D^{20}$-41.3 (c 1.0, CH_3OH); IR (KBr, ν_{max}, cm^{-1}): 3650, 1725,1586,1589, 1525; ^{1}H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) datas were showd in Table-1; ESIMS *m/z* 385 $[M+H]^+$; HRESIMS *m/z* 385.3342$[M+H]^+$ (calcd. for $C_{17}H_{21}O_{10}$, 385.3347).

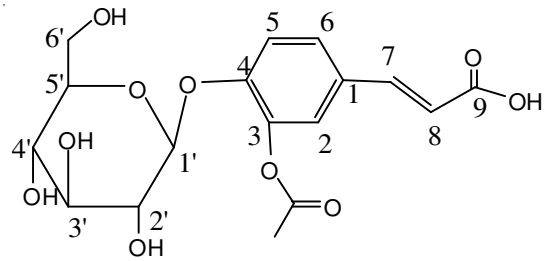

Fig. 1. Structure of **1**

The HRESIMS at *m/z* 384.3342 corresponded to the protonated molecular ion $[M+H]^+$ ($C_{17}H_{21}O_{10}$). The NMR spectra of **1** showed that the presence of one acetyl group (δ_H 2.20, 3H, s, δ_C 170.3, 20.7 q), one COOH group (δ_C 170.7), one CH=CH group (δ_H 6.32, δ_H 7.54, each 1H, d, J = 15.6; δ_C 117.6 d, 144.9 d), typical of an AB spin system, one glucopyranoside group (δ_H 4.80, 1H, d, J = 7.6 Hz, δ_C 103.4 d, 74.8 d, 77.5 d, 71.3 d, 78.3 d, 62.4 t) and one trisubstituted benzene (δ_H 7.23 d, J = 2 Hz, δ_H 7.06 d, J = 8.4 Hz; δ_H 7.30 dd J = 8.4, 2Hz; δ_C 129.9 s, 122.9 d, 140.6 s, 150.1 s, 115.5 d,127.7 d). In addition, the close resemblance of the ^{1}H and ^{13}C NMR spectra of 4-O-β-D-glucopyranosidecaffeic acid[4] and **1** except for absence of one acetyl group, which suggest that the

TABLE-1
^{1}H NMR AND ^{13}C NMR DATA OF COMPOUND **1** (CD_3OD)

C	δ_H	δ_C
1	-	129.9 s
2	7.23 (d, *J* = 2Hz)	122.9 d
3	-	140.6 s
4	-	150.1 s
5	7.06 (d, *J* = 8.4Hz)	115.5 d
6	7.30 (dd, *J* = 8.4, 2 Hz)	127.7 d
7	7.54 (d, *J* = 15.6Hz)	144.9 d
8	6.32 (d, *J* = 15.6Hz)	117.6 d
9		170.7 s
1'	4.80 (d, *J* = 7.6Hz)	103.5 d
2'		74.8 d
3'		77.5 d
4'		71.3 d
5'		78.3 d
6'		62.4 t
-$OCOCH_3$		170.3 s
-$OCOCH_3$	2.20 s	20.7 q

4-O-β-D-glucopyranosidecaffeic acid is a partial hydrolytic derivative of 1 and that the HO-3 was substituted for AcO-3. Correlations between H-1' and C-4, H-5 and C-3, H-5 and C-1, H-8 and C-1 in the HMBC spectrum (Fig. 2) suggested that the acetyl group and the glucopyranoside group could be assigned at C-3 and C-4, respectively. Consequently, the group assignments were achieved for **1** (3-acetyl-4-O-β-D-glucopyranosidecaffeic acid).

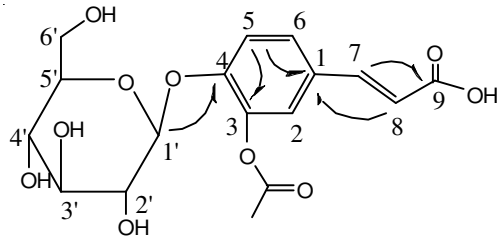

Fig. 2. Key HMBC (⌒) correlations of **1**

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