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A novel phenylpropanoid glycoside from *Callicarpa kwangtungensis* Chun

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Abstract

A novel phenylpropanoid glycoside, Callicarposide A has been isolated from the aerial parts of *Callicarpa kwangtungensis* Chun. The chemical structure is elucidated on the basis of spectral analysis.

Keywords: *Callicarpa kwangtungensis* Chun; Phenylpropanoid glycoside; Callicarposide A

The aerial parts of *Callicarpa kwangtungensis* Chun are used in Chinese herbal medicine for the treatment of pectoragia and haematemess. We report the isolation and structure elucidation of a novel phenylpropanoid glycoside, callicarposide A (compound **1**) that has been isolated from the aerial parts of *C. kwangtungensis* Chun.

The aerial parts of *C. kwangtungensis* Chun (2.05 kg) were purchased in Nanchang, and identified by pharmacia Yuan-guiping, JiangXi Provical Institute for Drug and Food Control. The voucher specimen (No. 201-A89-12-01) has been deposited at the JiangXi Provical Institute for Drug and Food Control. The *n*-BuOH-soluable part (100 g) of the water extract was repeatedly chromatographed over macroporous resin HP-20, Sephadex LH-20 column and preparative HPLC to give **1** (11 mg, 0.0055%).

Compound **1** was obtained as light yellowish gum, $[\alpha]_D^{20} - 23.3$ (c 0.0015, MeOH). In the (+)-TOF-MS of **1**, quasimolecular ion peaks were observed at *m/z* 777 $[M+Na]^+$, HR-TOF-MS (*m/z* 777.2245 $[M+Na]^+$) analysis revealed the molecular formula of **1** to be $C_{34}H_{42}O_{19}Na$ (calcd. 777.2212).

In the ^1H spectra of **1** exhibited the presence of two sets of AMX systems [δ_H 6.74 (d, 1H, 1.0 Hz), δ_H 6.70 (d, 1H, 8.0 Hz) and δ_H 6.66 (dd, 1H, 8.0/1.0 Hz) for the 2-(3,4-dihydroxyphenyl)-2-hydroxyethan-1-oxyl moiety; δ_H 7.03 (d, 1H, 1.5 Hz), δ_H 6.76 (d, 1H, 8.0 Hz) and δ_H 6.99 (dd, 1H, 8.0/1.5 Hz) for the caffeoyl moiety], two trans-olefinic protons [δ_H 6.20 (d, 1H, 15.5 Hz) and δ_H 7.50 (d, 1H, 15.5 Hz)] together with three anomeric protons δ_H 4.55 (d, 1H, 7.5 Hz) for β-glucose, δ_H 4.98 (s, 1H) for α-rhamnose and δ_H 4.77 (d, 1H, 3.0 Hz) for β-apiose. Comparism of the ^{13}C NMR spectral data with 2″-O-β-apiosylverbasco-side suggested that have three sugar moiety, anomeric carbon signals

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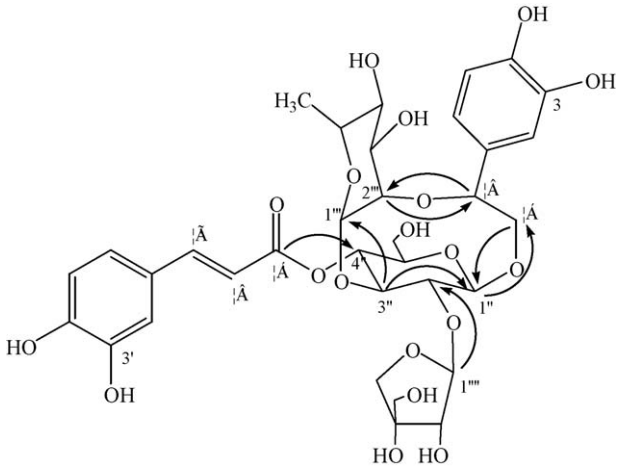

Fig. 1. Key HMBC correlations of compound **1**.

δ_C 96.5 for β-glucose, δ_C 100.2 for α-rhamnose and δ_C 109.0 for β-apiose, and the glucose is the core sugar with 2-(3,4-dihydroxyphenyl)-2-hydroxyethan-1-oxyl moiety located at C-1″ as well as the trans-caffeoyl moiety linked at C-4″ [1–3].

Acid hydrolysis of **1** with 5 mol/L HCl furnished L-rhamnose, D-glucose which were identified by HPLC analysis of the 1-phenyl-3-methyl-5-pyrazolone(PMP) derivatives [4]. From biogenetic considerations, apiose should be as D-sugar [5,7].

The structure of **1** was determined on the base of HMBC spectrum, the H-1 of apiose at δ_H 4.77 correlated with C-2 of the glucose at δ_C 80.2, the H-1 of rhamnose I at δ_H 4.98 correlated with C-3 of the glucose at δ_C 73.9, the H-4 of glucose at δ_H 4.84 correlated with C-α of the caffeoyl moiety at δ_C 165.4 [6], the H-1 of the glucose at δ_H 4.55 correlated with C-α of the 2-(3,4-dihydroxyphenyl)-2-hydroxyethan-1-oxyl moiety at δ_C 70.8, the H-α of the 2-(3,4-dihydroxyphenyl)-2-hydroxyethan-1-oxyl moiety at δ_H 3.47 and δ_H 3.94 correlated with C-1 of the glucose at δ_C 96.5, the H-2 of rhamnose I at δ_H 3.53 correlated with C-β of the 2-(3,4-dihydroxyphenyl)-2-hydroxyl-ethan-1-oxyl moiety at δ_C 75.9, furthermore in the H–H COSY spectrum, the H-2 of rhamnose at δ_H 3.53 correlated with H-β of the

Table 1
The ^{1}H NMR(500 MHz) and ^{13}C NMR (125 MHz) spectral data of **1** (DMSO-d6, δ ppm).

Aglycone	δc	δ_H	Sugar moiety	δc	δ_H
1	127.8		Glucose		
2	113.4	6.74 (d, 1H, 1.0 Hz)	1″	96.5	4.55 (d, 1H, 7.5 Hz)
3	144.9		2″	80.2	3.38 (dd, 1H, 7.5/10.0 Hz)
4	145.0		3″	73.9	4.06 (t, 1H, 10.0 Hz)
5	115.2	6.70 (d, 1H, 8.0 Hz)	4″	68.9	4.84 (t, 1H, 10.0 Hz)
6	117.0	6.66 (dd, 1H, 8.0/1.0 Hz)	5″	74.2	3.90 (m, 1H)
α	70.8	3.47 (m, 1H); 3.94 (m, 1H)	6″	63.0	3.30 (m, 2H)
β	75.9	4.57 (dd, 1H, 2.0/9.5 Hz)	Rhamnose		
Ester moiety			1‴	100.2	4.98 (s, 1H)
1′	125.3		2‴	70.3	3.53 (dd, 1H)
2′	114.7	7.03 (d, 1H, 1.5 Hz)	3‴	70.1	3.23 (m, 1H)
3′	148.5		4‴	71.3	3.09 (t, 1H, 9.0 Hz)
4′	145.3		5‴	68.7	3.41 (m, 1H)
5′	115.6	6.76 (d, 1H, 8.0 Hz)	6‴	17.8	1.02 (d, 3H, 6.5 Hz)
6′	121.4	6.99 (dd, 1H, 8.0/1.5 Hz)	Apiose		
α′	165.4		1⁗	109.0	4.77 (d, 1H, 3.0 Hz)
β′	112.9	6.20 (d, 1H, 15.5 Hz)	2⁗	75.7	3.74 (d, 1H, 3.0 Hz)
γ′	146.1	7.50 (d, 1H, 15.5 Hz)	3⁗	78.7	
			4⁗	73.3	3.81/3.56 (1H each, 10 Hz)
			5⁗	66.7	3.55 (m, 1H), 3.38 (m, 1H)

2-(3,4-dihydroxyphenyl)-2-hydroxyethan-1-oxyl moiety at δ_H 4.57, confirmed this conclusion. So the structure of compound **1** was shown in Fig. 1 (Table 1).

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