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Two New Phloroglucinol Glycosides from *Lysidice rhodostega* Hance

Song GAO, Shi Shan YU*, De Quan YU

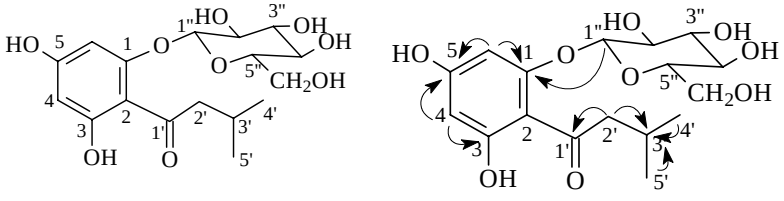
Institute of Materia Medica, Chinese Academy of Medical Sciences &
Peking Union Medical College, Beijing 100050

Abstract: Two new phloroglucinol glycosides, lysidiciside A (**1**) and lysidiciside B (**2**), were isolated from the roots of *Lysidice rhodostega* Hance. Their structures were determined as 1-[(3-methylbutyryl)phloroglucinol]- β-D- glucopyranoside (**1**), 1- [(3-methylbutyryl)phloroglucinol]- β-D-glucopyranosyl-5-*O*- β-D-glucopyranoside (**2**) on the basis of chemical and spectral analysis .

Keywords: *Lysidice rhodostega* Hance, phloroglucinol glycoside, lysidiciside A, lysidiciside B.

Lysidice rhodostega Hance is widely distributed in Guangxi, Guangdong, Yunnan and Guizhou province of China. It has long been used as a Chinese folk medicine for the treatment of fracture and hemorrhage [1]. No phytochemical investigation about this plant has been described in literature up to now. In this paper, we report two new phloroglucinol glycosides from the EtOAc extract of the roots of the title plant collected from Guangxi province.

Figure 1 Structure and key HMBC correlations of **1**



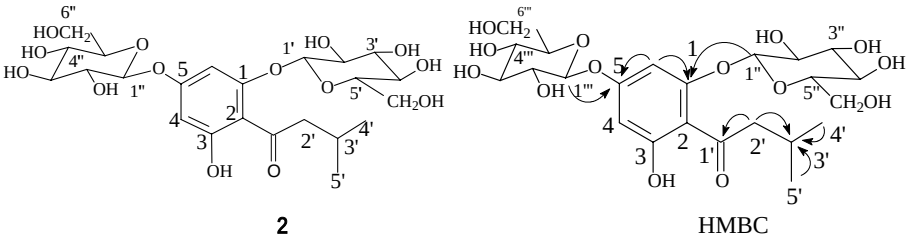
1

Compound **1** was obtained as white amorphous powder, mp112~115°C, $[\alpha]_D^{25}$ –83.6 (*c* 0.1, C_2H_5OH). The IR spectrum revealed absorption bands for hydroxyl (3467 cm^{-1}), aromatic group (1604, 1456 cm^{-1}) and conjugated carbonyl (1628 cm^{-1}) moieties. The molecular formula was established as $C_{17}H_{24}O_9$ by HRFABMS at *m/z* 373.1543 $[M+H]^+$ (calcd. for $C_{17}H_{24}O_9$, 373.1498).

Positive Molish reaction suggested that **1** was a glycoside. ^{13}C NMR spectrum analysis showed the presence of one hexosyl moiety for **1**. Acid hydrolysis of **1** yielded **3** as the aglycone that was determined as (3-methylbutyryl)phloroglucinol by comparison

* E-mail: yushishan@imm.ac.cn

Figure 2 Structure and key HMBC correlations of **2**



2 HMBC

Table 1 ^{1}H-NMR (500 MHz), ^{13}C-NMR (125 MHz) data of **1**, **2**, **3** (DMSO-d_6)

	δ_H *J* (Hz)			δ_C (DEPT)		
position	1	2	3	1	2	3
1				160.6 (s)	159.5 (s)	164.1 (s)
2				105.3 (s)	107.5 (s)	103.9 (s)
3				165.3 (s)	163.5 (s)	164.1 (s)
4	6.04 d (2.0)	6.13 d (2.0)	5.79 s	96.7 (d)	97.5 (d)	94.6 (d)
5				164.2 (s)	162.4 (s)	164.4 (s)
6	6.28 d (2.0)	6.31d (2.0)	5.79 s	94.2 (d)	94.2 (d)	94.6 (d)
1′				205.2 (s)	205.6 (s)	204.7 (s)
2′	3.03 dd (16.0, 7.5) 3.21 dd (16.0, 6.5)	2.86 dd (7.5, 16.0) 3.03 dd (6.0,16.0)	2.86 d (6.5)	52.2 (t)	52.5 (t)	51.8 (t)
3′	2.29 m	2.14 m	2.13 m	24.3 (d)	24.3 (d)	24.7 (d)
4′	0.96 d (6.5)	0.91 d (7.0)	0.91d (6.5)	22.7 (q)	22.6 (q)	22.6 (q)
5′	1.00 d (6.5)	0.87 d (6.5)	0.91d (6.5)	22.2 (q)	22.2 (q)	22.6 (q)
1″	5.12 d (7.5)	4.96 d (7.5)		100.6 (d)	100.3 (d)	
2″				73.2 (d)	73.2 (d)	
3″				77.2 (d)	77.1 (d)	
4″				69.4 (d)	69.8 (d)	
5″				76.8 (d)	76.7 (d)	
6″				60.4 (t)	60.7 (t)	
1‴		4.94 d (7.5)			99.2 (d)	
2‴					72.9 (d)	
3‴					77.0 (d)	
4‴					69.7 (d)	
5‴					76.4 (d)	
6‴					60.4 (t)	

of the NMR data (**Table 1**) with those of references [2, 3]. The sugar was identified as glucose by TLC comparison with an authentic sample, FABMS at *m/z* 211 $[M\text{-}Glu+H]^+$ and ^{13}C NMR data [4]. The large $^{3}J_{H1'', H2''}$ coupling constant (7.5 Hz) for the anomeric proton at δ 5.12 revealed the sugar wasβ-configuration.

Comparison of the carbon signals in ^{13}C NMR spectrum for **1** with those for **3**

disclosed a glycosilation shift for C-1 indicating the sugar moiety linked to C-1 position. Furthermore, the position of the sugar on the aglycone was confirmed by the HMBC experiment, which showed a long-range correlation between the anomeric proton at δ 5.12 (H-1″) and 160.6 (C-1). On the basis of these findings, the structure of **1** was characterized to be as 1-[(3-methylbutyryl)phloroglucinol]-β-D-glucopyranoside.

Compound **2** was obtained as yellow amorphous powder, mp 142~144° C, $[\alpha]_D^{25}$ -103.0 (*c* 0.2, MeOH). The IR spectrum displayed absorption bands for hydroxyl (3402 cm^{-1}), aromatic group (1590,1431 cm^{-1}) and conjugated carbonyl (1628 cm^{-1}) moieties. The molecular formula $C_{23}H_{34}O_{14}$ of **2** was deduced from HRFABMS at *m/z* 535.2020 $[M+H]^+$ (calcd. for $C_{23}H_{34}O_{14,}$ 535.2026.).

Acid hydrolysis of **2** also liberated **3** and glucose. Two anomeric carbon signals at δ 100.3, 99.2 in the ^{13}C NMR spectrum and two anomeric proton signals at δ 4.96, 4.94 in the ^1H NMR spectrum assigned two glucose moieties for **2**, which can be proved by FABMS data at *m/z* 373 $[M^+$-Glu+H$]^+$, 211 $[M^+$-Glu- Glu +H$]^+$ and ^{13}C- NMR data [4, 5]. The large $^3J_{H1'', H2''}$, $^3J_{H1''', H2'''}$ coupling constants (7.5 Hz) for the anomeric protons at δ 4.96, 4.94 showed the two sugars were both β-configuration.

When the ^{13}C NMR data of **2** were compared with those of **3**, glycosilation shifts were observed for C-1 and C-5. On the other hand, HMBC spectrum exhibited long-rang correlations between the anomeric proton at δ 4.96 (H-1″) and 159.5 (C-1), δ 4.94 (H-1‴) and 162.4 (C-5) indicating the two sugars attached on the aglycone *via* C-1 and C-5 hydroxyl groups. Thus, compound **2** was established as 1-[(3-methylbutyryl)-phloroglucinol]-β-D-glucopyranosyl-5-*O*-β-D-glucopyranoside.

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