

羽叶鬼灯檠中的单萜二糖苷

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摘要: 从羽叶鬼灯檠 (*Rodgersia pinnata* Franch.) 的根茎中分离得到 6 个单萜二糖苷, 它们的结构通过波谱方法分别鉴定为: (E)-3, 7-dimethyl-1-O-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl]-oct-2-en-7-ol (1), (E)-3, 7-dimethyl-1-O-[α -L-arabinofuranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl]-oct-2-en-7-ol (2), geranyl-1-O- α -L-arabinofuranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (3), geranyl-1-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (4), geranyl-1-O- β -D-xylopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (5), geranyl-1-O- α -L-arabinopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (6)。其中化合物 1 为新化合物, 单萜二糖苷类化合物系首次在该属中发现。

关键词: 羽叶鬼灯檠; 虎耳草科; 单萜二糖苷

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Monoterpene Disaccharide Glycosides from *Rodgersia pinnata*

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Abstract: From the rhizomes of *Rodgersia pinnata*, six monoterpene disaccharide glycosides were isolated and their chemical structures were determined as (E)-3, 7-dimethyl-1-O-[α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl]-oct-2-en-7-ol (1), (E)-3, 7-dimethyl-1-O-[α -L-arabinofuranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl]-oct-2-en-7-ol (2), geranyl-1-O- α -L-arabinofuranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (3), geranyl-1-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (4), geranyl-1-O- β -D-xylopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (5), geranyl-1-O- α -L-arabinopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (6) by spectral methods. Among them, compound 1 is a new monoterpene disaccharide glycoside. It is the first time that monoterpene disaccharide glycosides were isolated from the genus *Rodgersia*.

Key words: *Rodgersia pinnata*; Saxifragaceae; Monoterpene disaccharide glycosides

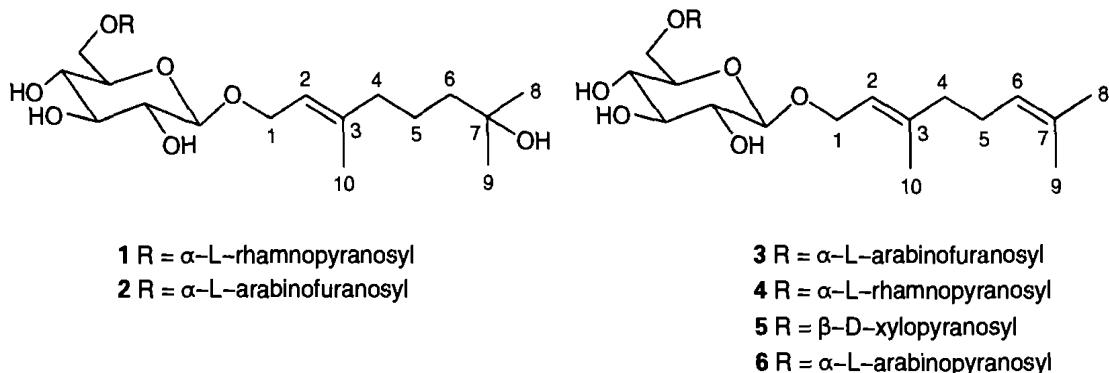
There are about 5 species and 3 variations in the genus *Rodgersia* Gray, which are mainly dis-

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tributed in East Asia. Some of them are used as traditional medicines which have anti-bacterial, anti-virus, antalgic, anti-inflammatory, hemostatic, anti-rheumatic and anti-tussive activities (Pan, 1994; Wu, 1990). Previous studies have indicated that tannins and related polyphenols are main constituents in this genus (Liu *et al*, 1995). In addition, many monoterpenoids and other volatile oil constituents were reported from this genus too (Kurihara *et al*, 1975; Shen *et al*, 1987; Zheng *et al*, 1988). Recently, several new diterpene lactones were also isolated from *R. aesculifolia* and *R. sambucifolia* (Zheng *et al*, 1998, 2002). However, the chemical constituents of *R. pinnata* haven't been reported until now. *In vitro* bioactivity screening we found that the extracts and fractions from *R. pinnata* showed strong inhibitory activities on Carbonic Anhydrase II, Cathepsin B and Cell Division Cycle 25 Phosphatase. In searching for the active constituents of this plant, we have studied the chemical constituents and finally found six monoterpene disaccharide glycosides (**1**–**6**) including a new one (**1**), which is the first time that monoterpene disaccharide glycosides were isolated from the genus *Rodgersia*. In this paper we would like to report the isolation and structure elucidation of these monoterpene disaccharide glycosides.



Results and discussion

Compound **1** was obtained as viscous solids with a molecular formula of C₂₂H₄₀O₁₁, which was determined by HRESI MS *m/z* 479.2506 [M-1]⁻, calcd. 479.2492. The IR spectrum showed absorptions at 3419 and 1638 cm⁻¹, which suggested the presence of hydroxyl and olefinic groups. The ¹H and ¹³C NMR spectra of **1** displayed signals of one α -L-rhamnopyranosyl at δ_c 102.1 (d), 72.1 (d), 72.3 (d), 74.0 (d), 69.7 (d), 18.0 (q) and δ_h 4.75 (1H, d, 1.5 Hz), one 6-substituted β -D-glucopyranosyl at δ_c 102.4 (d), 74.9 (d), 78.1 (d), 71.7 (d), 76.8 (d), 68.0 (t) and δ_h 4.27 (1H, d, 7.8 Hz). Other signals of three methyls (δ_c 29.2, 29.2, 16.4), four methylenes (δ_c 66.0, 44.2, 41.0, 23.4), one methine (δ_c 121.3) and two quarternary carbons (δ_c 142.4, 71.3), were deduced as 1-substituted (E)-3, 7-dimethyl-oct-2-en-1, 7-dioyl determined by ¹H-¹H COSY, HMQC and HMBC spectra. Therefore, the structure of **1** was elucidated as (E)-3, 7-dimethyl-1-O-[α -L-rhamnopyranosyl-(1→6)- β -D-glucopyranosyl]-oct-2-en-7-ol, which is a new monoterpene disaccharide glycoside.

With the same methods, the structures of compounds **2**–**6** were determined as (E)-3, 7-dime-

thyl-1-O-[α -L-arabinofuranosyl-(1 \rightarrow 6)- β -D-glucopyranosyl]-oct-2-en-7-ol (**2**) (Marinos *et al*, 1994), geranyl-1-O- α -L-arabinofuranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (**3**) (Williams *et al*, 1982), geranyl-1-O- α -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (**4**) (Williams *et al*, 1982), geranyl-1-O- β -D-xylopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (**5**) (Guo *et al*, 1993), geranyl-1-O- α -L-arabinopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside (**6**) (Yoshikawa *et al*, 1993).

Geranyl glycosides were mainly found in the genus *Vitis* (Williams *et al*, 1982), *Hovenia* (Yoshikawa *et al*, 1993), *Camellia* (Guo *et al*, 1993), *Ligustrum* (Tian *et al*, 1998), *Rosa* (Oka *et al*, 1998) and so on. And only a few (E)-3, 7-dimethyl-oct-2-en-1, 7-diyl glycosides were reported (Marinos *et al*, 1994). These monoterpene glycosides are aroma precursors in tea, flower and fruit aromas contributing to their floral fragrance (Yoshikawa *et al*, 1993; Oka *et al*, 1998). This is the first report of monoterpene disaccharide glycosides isolated from the genus *Rodgersia*.

Table 1 ^{13}C NMR spectral Data of compounds **1**–**6** in CD_3OD (100 MHz for δ_{C})

No.	1	2	3	4	5	6
1	66.0 (t)	66.3 (t)	66.4 (t)	65.9 (t)	66.6 (t)	66.5 (t)
2	121.3 (d)	121.4 (d)	121.4 (d)	121.3 (d)	121.5 (d)	121.5 (d)
3	142.4 (s)	142.2 (s)	142.1 (s)	142.3 (s)	141.9 (s)	141.8 (s)
4	41.0 (t)	41.0 (t)	40.6 (t)	40.7 (t)	40.6 (t)	40.7 (t)
5	23.4 (t)	23.3 (t)	27.5 (t)	27.4 (t)	27.4 (t)	27.4 (t)
6	44.2 (t)	44.2 (t)	125.1 (d)	125.0 (d)	125.1 (d)	125.1 (d)
7	71.3 (s)	71.3 (s)	132.5 (s)	132.5 (s)	132.5 (s)	132.5 (s)
8	29.2 (q)	29.2 (q)	25.8 (q)	25.9 (q)	25.8 (q)	25.9 (q)
9	29.2 (q)	29.2 (q)	17.8 (q)	17.8 (q)	17.7 (q)	17.8 (q)
10	16.4 (q)	16.4 (q)	16.5 (q)	16.5 (q)	16.6 (q)	16.6 (q)
Glc-1	102.4 (d)	102.6 (d)	102.8 (d)	102.3 (d)	102.9 (d)	102.9 (d)
Glc-2	74.9 (d)	74.9 (d)	75.0 (d)	74.9 (d)	74.8 (d)	75.0 (d)
Glc-3	78.1 (d)	77.9 (d)	78.1 (d)	78.1 (d)	78.0 (d)	77.9 (d)
Glc-4	71.7 (d)	71.9 (d)	72.1 (d)	71.7 (d)	71.6 (d)	71.5 (d)
Glc-5	76.8 (d)	76.7 (d)	76.7 (d)	76.8 (d)	76.9 (d)	76.8 (d)
Glc-6	68.0 (t)	68.0 (t)	68.1 (t)	68.0 (t)	69.8 (t)	69.4 (t)
Rha-1	102.1 (d)			102.1 (d)		
Rha-2	72.1 (d)			72.1 (d)		
Rha-3	72.3 (d)			72.3 (d)		
Rha-4	74.0 (d)			74.0 (d)		
Rha-5	69.7 (d)			69.7 (t)		
Rha-6	18.0 (q)			18.0 (q)		
Ara(f)-1		109.9 (d)	110.0 (d)			
Ara(f)-2		83.1 (d)	83.1 (d)			
Ara(f)-3		78.8 (d)	79.0 (d)			
Ara(f)-4		85.7 (d)	86.1 (d)			
Ara(f)-5		63.0 (t)	63.1 (t)			
Xyl-1				105.5 (d)		
Xyl-2				75.0 (d)		
Xyl-3				77.6 (d)		
Xyl-4				71.2 (d)		
Xyl-5				66.8 (t)		
Ara(p)-1					105.1 (d)	
Ara(p)-2					72.3 (d)	
Ara(p)-3					74.1 (d)	
Ara(p)-4					69.4 (d)	
Ara(p)-5					66.7 (t)	

Table 2 ^1H NMR spectral data of Compounds 1–6 in CD_3OD

No.	1 (400 MHz for δ_{H})	2 (500 MHz for δ_{H})	3 (500 MHz for δ_{H})	4 (500 MHz for δ_{H})	5 (500 MHz for δ_{H})	6 (500 MHz for δ_{H})
1	4.29 (dd, 7.0, 11.8) 4.23 (dd, 7.9, 11.8)	4.31 (dd, 6.2, 11.9) 4.23 (dd, 7.7, 11.9)	4.31 (dd, 6.3, 11.9) 4.22 (dd, 7.7, 11.9)	4.28 (dd, 6.4, 12.2) 4.23 (dd, 8.0, 12.0)	4.34 (dd, 6.5, 11.4) 4.21 (dd, 7.6, 11.9)	4.32 (dd, 6.8, 12.3) 4.20 (dd, 7.4, 11.8)
2	5.37 (t, 6.5) 2.05 (t, 7.0)	5.37 (t, 6.6) 2.04 (t, 7.2)	5.36 (m) 2.08 (m)	5.36 (t, 6.5) 2.08 (m)	5.36 (t, 7.2) 2.08 (m)	5.36 (t, 6.9) 2.08 (m)
4	1.50 (m)	1.50 (m)	2.08 (m)	2.08 (m)	2.08 (m)	2.08 (m)
5	1.41 (m)	1.41 (m)	5.10 (m)	5.10 (m)	5.10 (t, 6.9)	5.10 (t, 6.3)
6	1.17 (s)	1.17 (s)	1.67 (s)	1.67 (d, 0.7)	1.67 (s)	1.67 (s)
8	1.17 (s)	1.17 (s)	1.60 (s)	1.60 (s)	1.60 (s)	1.60 (s)
9	1.17 (s)	1.17 (s)	1.69 (s)	1.69 (s)	1.68 (s)	1.68 (s)
10	1.69 (s)	4.28 (d, 7.9)	4.28 (d, 7.8)	4.26 (d, 7.8)	4.28 (d, 7.9)	4.28 (d, 7.9)
Glc-1	4.27 (d, 7.8)	3.17 (dd, 8.2, 8.7)	3.17 (t, 8.4)	3.17 (dd, 7.9, 9.0)	3.17 (m)	3.18 (m)
Glc-2	3.18 (t, 8.4)	3.34 (t, 8.9)	3.34 (m)	3.30 (m)	3.32 (m)	3.35 (m)
Glc-3	3.34 (m)	3.28 (t, 9.3)	3.28 (m)	3.26 (t, 9.2)	3.32 (m)	3.36 (m)
Glc-4	3.28 (m)	3.41 (ddd, 2.3, 6.0, 9.5)	3.40 (ddd, 2.3, 5.9, 9.5)	3.30 (m)	3.39 (m)	3.40 (m)
Glc-5	3.38 (m)	3.97 (dd, 1.5, 11.1)	4.02 (dd, 2.2, 11.1)	3.97 (dd, 1.7, 11.1)	4.08 (dd, 1.9, 11.4)	4.09 (dd, 2.0, 11.3)
Glc-6	3.60 (dd, 6.2, 11.2)	3.60 (dd, 5.8, 11.0)	3.60 (dd, 5.9, 11.0)	3.59 (dd, 6.1, 11.1)	3.74 (dd, 5.5, 11.5)	3.73 (dd, 5.2, 11.3)
Rha-1	4.75 (d, 1.5)	3.84 (dd, 1.6, 3.3)	4.96 (d, 1.0)	4.96 (s)	4.31 (d, 7.6)	
Rha-2	3.65 (dd, 3.4, 9.5)	3.99 (dd, 1.3, 3.3)	3.99 (m)	3.65 (dd, 3.5, 9.5)	3.19 (m)	
Rha-3	3.36 (m)	3.82 (dd, 3.3, 6.0)	3.82 (m)	3.36 (t, 9.0)	3.32 (m)	
Rha-4	3.65 (dd, 6.1, 9.5)	3.96 (ddd, 3.3, 5.7, 5.7)	3.96 (dd, 3.4, 5.5, 5.5)	3.65 (dd, 6.0, 9.5)	3.48 (ddd, 5.4, 9.0, 9.9)	
Rha-5	1.26 (d, 6.3)	3.74 (dd, 3.3, 11.9)	3.74 (dd, 3.3, 11.9)	1.26 (d, 6.3)	3.85 (dd, 5.3, 11.5)	
Ara(f)-1					3.19 (m)	
Ara(f)-2					3.32 (m)	
Ara(f)-3					3.48 (ddd, 5.4, 9.0, 9.9)	
Ara(f)-4					3.85 (dd, 5.3, 11.5)	
Ara(f)-5					3.19 (m)	
Xyl-1					4.30 (d, 6.8)	
Xyl-2					3.59 (dd, 6.8, 8.8)	
Xyl-3					3.52 (dd, 4.0, 8.8)	
Xyl-4					3.80 (m)	
Xyl-5					3.86 (dd, 3.2, 12.4)	
Ara(p)-1					3.54 (dd, 1.6, 12.4)	
Ara(p)-2						
Ara(p)-3						
Ara(p)-4						
Ara(p)-5						

Experimental

General Optical rotations were taken on a Horiba SEAP-300 polarimeter. IR spectra (KBr) were measured on a Bio-Red FTS-135 infrared spectrophotometer. UV spectra (MeOH) were run on a 2401PC UV spectrophotometer. ¹H, ¹³C NMR and 2D NMR spectra were recorded on a Bruker AM-400 or a DRX-500 NMR spectrometer with TMS as internal standard and CD₃OD as solvent. MS data were obtained on a VG Autospec-3000 spectrometer. Silica gel (200–300 mesh) for column chromatography and TLC Silica gel plates were bought from the Qindao Marine Chemical Factory, Qindao, China. Gel Sephadex LH-20 and RP-18 were the products of the Pharmacia AB Laboratory Separation Division, Uppsala, Sweden, and Merck Company, Germany, respectively.

Plant material The rhizomes of *R. pinnata* Franch. were collected in Shangri-la, Yunnan Province of China in September 2002. The plant was identified by associated Professor Wang Zong-Yu, Kunming Institute of Botany, Chinese Academy of Sciences. The voucher specimen was deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation The dried and powdered rhizomes of *R. pinnata* (7.0 kg) were extracted with 95% EtOH at room temperature. The extracts were concentrated in vacuo. The residues were dissolved in H₂O and partitioned with petroleum ether, EtOAc and n-BuOH successively. When partitioned the EtOAc extracts, there were some floccules which were collected solely. The floccules (190 g) were subjected to column chromatography on a Silica gel column and eluted with acetone and MeOH to give two fractions (I–II). Fraction I was further purified by column chromatography on Silica gel column with CHCl₃-MeOH, CHCl₃-MeOH-H₂O and CHCl₃-acetone, and Sephadex LH-20 column with MeOH, and RP-18 column with aqueous methanol repeatedly, and to afford compounds 1 (200 mg), 2 (160 mg), 3 (220 mg), 4 (350 mg), 5 (65 mg) and 6 (32 mg).

Compound (1), C₂₂H₄₀O₁₁; viscous solids. [α]_D^{24.3} – 57.0° (c 0.383, MeOH); IR ν_{max}^{KBr} cm⁻¹: 3419, 2937, 1638, 1452, 1382, 1137, 1046, 981, 912, 810; UV λ_{max}^{MeOH} nm (log ε): 205 (3.99); Negative ion FAB-MS m/z (%): 479 [M-H]⁻ (100), 323 (5), 205 (26), 143 (23); HRESI MS m/z: 479.2506, calcd. 479.2492; ¹H and ¹³C NMR data see Tables 1 and 2.

Compound (2), C₂₁H₃₈O₁₁; viscous solids; [α]_D^{24.3} – 82.5° (c 0.305, MeOH); Negative ion FAB-MS m/z (%): 465 [M-H]⁻ (100), 311 (24), 191 (61), 149 (44), 119 (32); ¹H and ¹³C NMR data see Tables 1 and 2.

Compound (3), C₂₁H₃₆O₁₀; viscous solids; [α]_D^{24.3} – 84.8° (c 0.228, MeOH); Negative ion FAB-MS m/z (%): 447 [M-H]⁻ (100), 311 (11), 191 (24), 149 (17), 119 (12); ¹H and ¹³C NMR data see Tables 1 and 2.

Compound (4), C₂₂H₃₈O₁₀; viscous solids; [α]_D^{24.3} – 55.6° (c 0.384, MeOH); Negative ion FAB-MS m/z (%): 461 [M-H]⁻ (100), 325 (8), 265 (8), 205 (22), 163 (20), 119 (14), 71 (27); ¹H and ¹³C NMR data see Tables 1 and 2.

Compound (5), C₂₁H₃₆O₁₀; viscous solids. [α]_D^{24.3} – 40.8° (c 0.200, MeOH); Negative ion FAB-MS m/z (%): 447 [M-H]⁻ (100), 311 (6), 191 (5), 149 (9); ¹H and ¹³C NMR data see Tables 1 and 2.

Compound (6), C₂₁H₃₆O₁₀; viscous solids. [α]_D^{24.3} – 43.2° (c 0.158, MeOH); Negative ion FAB-MS m/z (%): 447 [M-H]⁻ (100), 311 (9), 191 (25), 149 (28); ¹H and ¹³C NMR data see Tables 1 and 2.

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