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FLAVONOID AND CYCLOARTANE GLYCOSIDES FROM SEEDS OF *Koelreuteria paniculata*

M. G. Sutiashvili,[1] M. D. Alaniya,[1*] V. D. Mshvildadze,[1] A. V. Skhirtladze,[1] A. Pichette,[2] and S. Lavoie[2]

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In continuation of research on the chemical components of *Koelreuteria paniculata* Laxm. (Sapindaceae L.), two compounds **1** and **2** were obtained in addition to the previously isolated compound saponin B [1]. Herein we present proof of the structures based on UV, IR, PMR, ^{13}C NMR, HSQC, and HMBC spectroscopic data and mass spectrometry.

Compound 1, yellowish powder, positive Shinoda reaction [2] and negative Bryant [3]. IR spectrum (KBr, ν_{max}, cm^{-1}): 3600 (OH), 1694 and 1650 (C=O). UV spectrum (λ_{max}, nm): 360, 255, 314sh. Mass spectrum *m*/*z*: 1209.3 [M – H]$^-$; 1063 [M – 146 – H]$^-$ (cleavage of *p*-coumaric acid); 1047 [M – 162 – H]$^-$ (cleavage of D-glucose); 917 [M – (146 + 146) – H]$^-$; 777 [M – (286 + 146) – H]$^-$; 739 [M – (162 × 2) – 146]$^-$; 593 [M – (146 × 2) + (162 × 2) – H]$^-$; 285 [M – (146 × 3) + (162 × 3) – H]$^{--}$; 147 (*p*-coumaric acid). $C_{54}H_{66}O_{31}$.

Acid hydrolysis of **1** produced the genin (20%) with mp 280–282°C that was identified as kaempferol [4]. Paper chromatography (PC) and LC of the carbohydrate part of the hydrolysate identified L-rhamnose, D-glucose, and *p*-coumaric acid in a 2:3:1 ratio.

According to UV, PMR, and ^{13}C NMR spectra (Table 1), the carbohydrate units in **1** were located on the kaempferol C-3 and C-7 positions. The SSCC of the anomeric protons were consistent with the pyranose form of the carbohydrates. Monosaccharides of the D-series had the $^4C_1$-conformation and the β-configuration; of the L-series, the $^1C_4$-conformation and the α-configuration.

The HMBC spectrum showed correlation peaks between resonances of anomeric L-rhamnose protons with C-7 and C-3 of the genin. Thus, the L-rhamnose was terminal; the two D-glucoses, end; and the *p*-coumaric acid, located within the chain of the tetraose and bonded to D-glucose C-6 which was bonded to L-rhamnose C-3″.

A comparison of the results with the literature [5] identified **1** as kaempferol-7-*O*-α-L-rhamnopyranosyl, 3-*O*-α-L-[(2″→1‴)-*O*-β-D-glucopyranosyl), (3″→1⁗)-*O*-β-D-(6⁗→9⁗⁗)-*p*-coumaroylglucopyranosyl, (4″→1⁗⁗)-β-D-glucopyranosyl]rhamnopyranoside.

Compound 2. MW 664 g/mol, $C_{37}H_{60}O_{10}$, mp 225–227°C ($CHCl_3$:MeOH, 1:1). IR spectrum (KBr, ν_{max}, cm^{-1}): 3363 (OH), 3050 (CH_2 of cyclopropane ring), 1755, 1245 (ester). Mass spectrum *m*/*z*: 687 [M + Na]$^-$; 627 [M + Na – 60]$^-$ (cleavage of acetyl); 495 [M + Na – 60 – 132]$^-$ (cleavage of D-xylose).

Acid hydrolysis of **2** produced a genin with mp 196–197°C (MeOH). A solution of the genin in Me_2CO in the presence of H_2SO_4 did not form a monoacetonide, indicating the absence of an α-diol group in the side chain [6]. The compound was identified as cyclogalegigenin [7]. PC of the carbohydrate part of the hydrolysate detected D-xylose.

Compound **2** with KOH solution (0.5%) at room temperature gave a glycoside with mp 253–255°C that was identified as cyclogaleginoside B [7]. This indicated that an acetyl was present in the studied glycoside.

Judging from the ^{13}C NMR spectrum and HMBC spectral analysis, the carbohydrate part of glycoside **2** was located on C-3 of the genin (Table 2). The SSCC of the anomeric proton of the monosaccharide was consistent with the β-configuration and the pyranose form of D-xylose. The chemical shift of C-2 of D-xylose in the ^{13}C NMR spectrum also indicated that the acetyl was bonded to the same position.

An analysis of the results characterized **2** as 3-*O*-β-D-(2′-*O*-acetyl)-xylopyranosyl-20*S*,24*R*-epoxycycloartan-3β,6α,16β,25-tetraol (cyclogaleginoside A) [7].

Glycosides **1** and **2** were isolated from *K. paniculata* for the first time.

1) I. G. Kutateladze Institute of Pharmaceutical Chemistry, Tbilisi, fax: (99532) 25 00 26, e-mail: merialania@yahoo.com; 2) Department des Sciences Fundamentales, Universite du Quebec a Chicoutimi, Quebec, Canada G7H 2B1, Translated from *Khimiya Prirodnykh Soedinenii*, No. 2, March–April, 2013, pp. 333–334. Original article submitted February 16, 2012.

TABLE 1. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR Spectra of Glycoside **1** (CD_3OD, δ, ppm, J/Hz)

C atom	δ_C	δ_H	C atom	δ_C	δ_H
Aglycon			Glucose 2		
2	158.7		Glc-1‴→3″-Rha		
3	135.3		1‴	105.0	4.79 (1H, d, J = 8.0)
4	179.0		2‴	74.8	
5	162.0		3‴	77.8	
6	100.8	6.44 (1H, d, J = 1.9)	4‴	72.3	
7	163.3		5‴	75.8	
8	95.5	6.57 (1H, d, J = 1.7)	6‴	65.4	
9	157.5		Glucose 3		
10	107.3		Glc-1⁗→4″-Rha		
1′	122.2		1⁗	103.6	4.71 (1H, d, J = 8.0)
2′, 6′	131.9	7.78 (2H, d, J = 8.6)	2⁗	75.4	
3′, 5′	116.7	7.04 (2H, d, J = 8.6)	3⁗	78.2	
4′	161.2		4⁗	70.7	
Rhamnose 1″ on C-3			5⁗	77.3	
1″	100.8	5.72 (1H, br.s)	6⁗	62.4	
2″	80.8		Rhamnose 2 on C-7		
3″	80.2		1	99.5	5.61 (1H, br. s.)
4″	78.1		2	71.4	4.12
5″	70.9		3	71.7	3.92 (dd, J = 9.5; 3.7)
6″	17.8	0.98 (3H, d, J = 6.2)	4	73.3	3.54
Glucose 1			5	71.0	3.70
Glc-1‴→2″-Rha			6	18.0	1.31 (3H, d, J = 6.0)
1‴	105.7	4.55 (1H, d, J = 8.0)	*p*-Coumaric acid		
2‴	74.8		coumaroyl -9⁗→6‴-Glc		
3‴	77.3		1⁗	126.4	7.01 (2H, d, J = 8.5)
4‴	71.4		2, 6⁗	130.3	6.33 (2H, d, J = 8.5)
5‴	77.4		3, 5⁗	116.3	
6‴	62.2		4⁗	160.2	7.50 (1H, d, J = 15.9)
			7⁗	146.8	6.21 (1H, d, J = 15.9)
			8⁗	114.8	
			9⁗	169.4	

TABLE 2. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR Spectra of Glycoside **2** (CD_3OD, δ, ppm, J/Hz)

C atom	δ_C	δ_H	C atom	δ_C	δ_H
1	32.65		20	86.90	
2	29.60		21	28.80	
3	88.10	3.18 (dd, J = 8.5; 1.4)	22	34.70	
4	42.70		23	26.17	
5	53.80		24	85.05	3.90 (dd, J = 9; 5)
6	68.40	3.45 (td, J = 18.8)	25	70.10	
7	37.80		26	27.50	
8	46.30		27	28.10	
9	20.20		28	20.30	
10	29.60		29	29.20	
11	26.15		30	16.10	
12	33.70		$\underline{CO}$-CH_3	170.02	–
13	45.50		CO-$\underline{CH_3}$	19.70	2.10 s
14	46.30		Xylose		
15	47.40		1′	104.80	4.19 (d, J = 7.5)
16	73.30	4.65 (m, H-16, H-2′)	2′	76.02	
17	58.80		3′	75.00	
18	21.60		4′	71.31	
19	30.20	0.38; 0.54 (d, J = 4.1)	5′	66.65	

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