LUTEOLIN DIGLUCURONIDE FROM *Perilla nankinensis*

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We have previously reported the isolation of flavonoids from leaves of *Perilla nankinensis* and established the structure of apigenin diglucuronide [1]. In continuation of the separation of the total extracts, we isolated glycoside **1**, a finely crystalline light yellow powder, mp 184-186°C (dec.), $[\alpha]_D^{20}$ -32.5° (*c* 0.05, MeOH), $[M]^+$ 639, $C_{27}H_{26}O_{18}$.

The UV spectrum of **1** (λ_{max} 268 and 336 nm) is typical of flavones, as is the IR spectrum (KBr, ν_{max}, cm^{-1}): 3250 (OH) and 1656 (γ-pyrone C=O). However, there is an absorption band in the IR spectrum that is characteristic of carboxylic acids at 1740 cm^{-1} in addition to that at 1650-1630 cm^{-1}.

The PMR spectrum contains signals for 9 aromatic and 10 sugar protons [2]. These include the C-3 proton that is observed as a singlet at 6.83 ppm, the chelate hydroxyl (5-OH) at δ 12.97 ppm, and two hydroxyls at 9.88 and 9.37 ppm (4′-OH and 3′-OH), respectively (Table 1). Signals at 6.05 and 5.56 ppm with SSCC 7.5 Hz each are consistent with the presence of two anomeric protons.

The absorption band at 1740 cm^{-1} in the IR spectrum is consistent with glucuronic acid in the flavone. Furthermore, a 1H doublet at 4.94 and 4.75 ppm (J = 9.0 Hz each) is characteristic of H-5″ and H-5‴ of D-glucuronic acid [3].

Hydrolysis of **1** [4] gives an aglycon of formula $C_{15}H_{10}O_6$ with mp 342-344°C and D-glucuronic acid. Judging from the yield of genin (~53%) and the PMR data for the glycoside, there should be at least two molecules of glucuronic acid.

The physicochemical properties of the aglycon and its acetyl derivative were compared with an authentic sample of luteolin and identified the aglycon as 5,7,3′,4′-tetrahydroxyflavone, luteolin [5].

The ^{13}C NMR spectrum showed that the carbohydrate part was bonded to aglycon C-7 (Table 1). The signal for C-7 shifts to strong field by 1.15 ppm on going from the aglycon (**2**) to the glycoside (**1**) whereas the signals for C-6 and C-8 undergo paramagnetic shifts of 5.20 and 0.17 ppm, respectively. The chemical shifts of C-1 and C-2 of the carbohydrate part are similar to luteolin diglucuronide [3], which confirms that the second molecule of glucuronic acid is located at the C-2″ position.

Therefore, the glycoside is 5,3′,4′-trihydroxy-7-*O*-β-D-glucuronyl-(2→1)-glucuronopyranosylflavone or luteolin diglucuronide [3]. The structure is analogous to that of the compound isolated previously from *Perilla ocimoides* [3].

TABLE 1. PMR and ^{13}C NMR Spectra of Luteolin-7-diglucuronide (**1**) and Luteolin (**2**) (δ, ppm, J/Hz, DMSO-d_6)

C atom	**1**		**2**	
	δ_C	δ_H	δ_C	δ_H
2	165.21		164.16	
3	103.98	6.83 s	105.34	6.48 s
4	182.79		183.10	
5	157.75	12.97 s	158.72	12.90 s
6	100.80	7.13 d (2.0)	95.60	6.20 d (2.0)
7	163.68		164.83	10.8 s
8	95.85	7.14 d (2.0)	95.68	6.50 d (2.0)
9	162.66		162.0	
10	106.79		105.1	

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TABLE 1. (continued)

C atom	1		2	
	δ_C	δ_H	δ_C	δ_H
1′	122.98		122.98	
2′	114.69	7.85 d (2.0)	114.69	7.30 d (9.0)
3′	147.64	9.37 s	146.64	
4′	151.76	9.88 s	150.76	
5′	116.76	7.20 d (8.5)	116.76	6.8 d (8.5)
6′	119.60	7.42 d (8.5)	119.60	7.30 dd (8.5; 2.0)
1″	100.31	6.05 d (7.5)		
2″	84.14	4.58 dd (9.0; 7.5)		
3″	76.98	4.56 t (9.0)		
4″	72.58	4.73 t (9.0)		
5″	77.55	4.95 d (9.0)		
6″	171.91			
1‴	106.97	5.56 d (7.5)		
2‴	76.20	4.27 dd (7.5; 9.0)		
3‴	77.81	4.30 t (9.0)		
4‴	73.32	4.60 t (9.0)		
5‴	78.19	4.75 t (9.0)		
6‴	172.49			

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