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A Flavonol Glycoside from *Smilax glabra*

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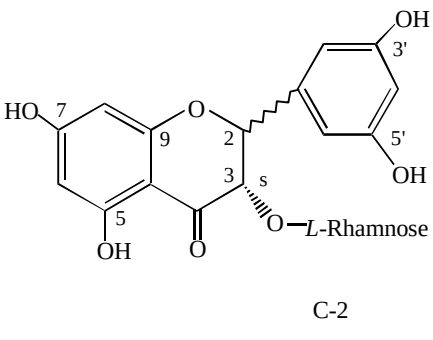
Abstract: A new flavonol glycoside, named neosmitilbin was isolated form the rhizome of *Smilax glabra*. Its structure and absolute configuration were elucidated on the basis of spectroscopic studies.

Keywords: *Smilax glabra*, neosmitilbin, flavonol.

The rhizome of *Smilax glabra* (Liliaceae) is a well-known traditional chinese drug and has been extensively used to treat syphilis, acute bacillary dysentery, acute and chronic nephritis, *etc.*[1]. In our previous studies on this plant[2,3], we have characterized a new flavonol rhamnoside (smitilbin), five new phenylpropanoid glycosides (smiglaside A-E), together with 6 known compounds and found that flavanoids possess potent activity in protecting immunological hepatocyte damage. In the continuing study, we isolated a new flavonol glycoside, neosmitilbin **1**. The present communication describes the structure elucidation of this new compound.

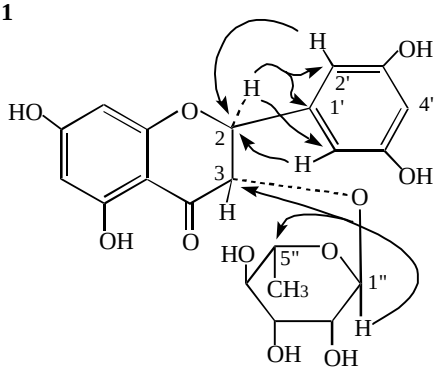
Compound **1** was obtained as colorless needles, mp 167-168°C, $[\alpha]_D^{25}$-288.7 (*c* 0.1, MeOH), IR (KBr) ν cm^{-1}: 3364 (OH), 2630, 1643 (C=O), 1258, 1029 and 824. The negative ion FAB-MS showed the quasi-molecular ion peak at *m/z* 449 [M-H] and its molecular formula was determined to be $C_{21}H_{22}O_{11}$ [(M-H) 449.1107, calcd. as

Chart 1



C-2

Compound **1** (2*S*): $C_6H_3(OH)_2$
Smitilbin (2*R*): $C_6H_3(OH)_2$



Important long-range correlations observed in FG-HMBC experiment

$C_{21}H_{21}O_{11}$, 449.1084] by high resolution FAB-MS. The UV [(MeOH) λ_{max} (log ε) nm: 227 (4.203), 291 (4.312)] and ^{1}H-NMR spectra suggested that compound **1** was a flavonol and possessed a hexose. On acid hydrolysis, compound **1** afforded rhamnose that was identified as α-L-rhamnose by detailed analysis of NMR data.

Extensive analysis of the ^{1}H-NMR data of **1** (**Table 1**) with aid of ^{1}H-^{1}H COSY indicated that **1** possessed 5, 7-disubstituted A-ring and 3′, 5″-disubstituted B-ring, which was identical with smitilbin[2]. However, two oxygen-bearing methine protons assignable to 2 and 3 positions of C-ring (δ_H 4.98, 1H, d, *J*=11.4Hz, 2-H; 4.62, 1H, d, *J*=11.4Hz, 3-H) showed a big *J* value in comparison with that of smitilbin (*J*=2.0Hz, 2*R*, 3*S*), revealing 2, 3 protons to be *trans*. Furthermore, the remarkable upfield shifts of H-5″ and H_3-6″ of rhamnose due to the aromatic shielding effect contributed by B-ring, and negative $[\alpha]_D$ led us to conclude the configurations at C2 and C3 to be 2*S*, 3*S* [4-7].

In order to determine the linkage of rhamnose and aglycone, FG (field gradient) HMBC experiment was conducted. A clear correlation between anomeric proton (δ_H 5.15, d, 1H, *J*=1.5) and C-3 (δ_C 76.92) deduced that rhamnose was connected to C-3 of aglycone. Other important correlations were depicted in **Chart 1** by arrows.

Based on the above findings, the structure of **1** was determined as represented in **Chart 1**, a diastereomer of smitilbin, and named neosmitilbin.

Table 1 ^{1}H- and ^{13}C-NMR spectral data of compound **1** in CD_3OD

No.	δ_C	δ_H (J in Hz)	No.	δ_C	δ_H (J in Hz)
2	83.70	4.98, 1H, d, *J*=11.4	3′	147.48	------
3	76.92	4.62, 1H, d, *J*=11.4	4′	116.28	6.80, 1H, s
4	197.67	------	5′	146.66	------
5	165.52	------	6′	121.00	6.80, 1H, s
6	96.32	5.88, 1H, d, *J*=2.0	1″	102.88	5.15, 1H, d, *J*=1.5
7	168.94	------	2″	71.94	4.00, 1H, dd, *J*=3.3, 1.5
8	97.46	5.91, 1H, d, *J*=2.0	3″	71.94	3.38, 1H, dd, *J*=9.6, 3.3
9	164.35	------	4″	73.43	3.19, 1H, t, *J*=9.6
10	102.04	------	5″	70.32	2.29, 1H, m
1′	129.98	------	6″	17.92	0.90, 3H, d, *J*=6.3
2′	115.47	6.97, 1H, s			

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