

Short Note

## A New Flavonoid Glycoside from *Salix denticulata* Aerial Parts

Usha Rawat, Sushma Semwal, Deepak Kumar Semwal \*, Ruchi Badoni and Amita Bamola

Department of Chemistry, H. N. B. Garhwal University, Srinagar-246174, U.K., India

\* Author to whom correspondence should be addressed; E-Mail: dr\_dks.1983@yahoo.co.in.

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**Abstract:** A new flavonoid glycoside (**1**) has been isolated from the aerial parts of *Salix denticulata* (Salicaceae) together with five known compounds,  $\beta$ -sitosterol, 2,6-dihydroxy-4-methoxy acetophenone, eugenol-1-*O*- $\beta$ -D-glucopyranoside, 1-*O*- $\beta$ -D-(3'-benzoyl) salicyl alcohol and luteolin-7-*O*- $\beta$ -D-glucopyranosyl-(1-6)-glucopyranoside. The structure of **1** was elucidated as 2',5-dihydroxy-3'-methoxyflavone-7-*O*- $\beta$ -D-glucopyranoside by means of chemical and spectral data including 2D NMR studies.

**Keywords:** *Salix denticulate*; Salicaceae; flavonoid glycoside

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### 1. Introduction

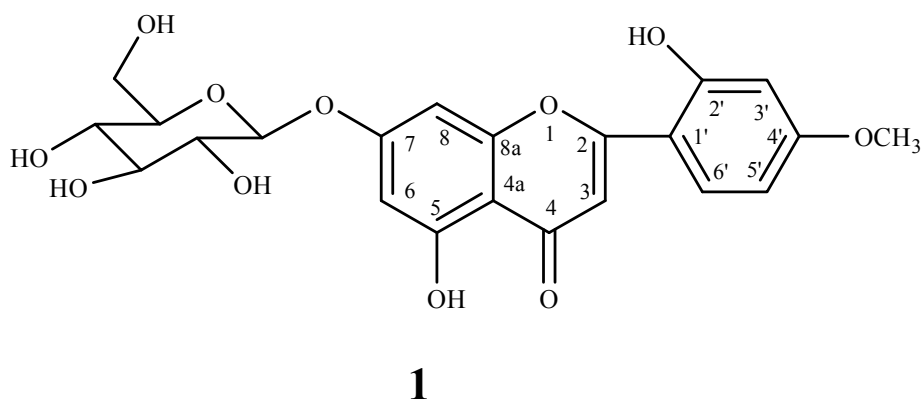
*Salix denticulata* which belongs to the Salicaceae family is a deciduous shrub indigenous to Central Himalayas (3000 meter) of India and is well known for its medicinal importance [1]. Previous studies on the plants of this genus led to isolation and elucidation of different compounds such as terpenoids [2], catechins [3], lignans [4], flavones [5,6] and other phenolic compounds [7]. This paper illustrates the isolation and structure revelation of a novel flavonoid glycoside (**1**) from the aerial parts of *S. denticulata* with the help of modern spectroscopic methods.

### 2. Results and discussion

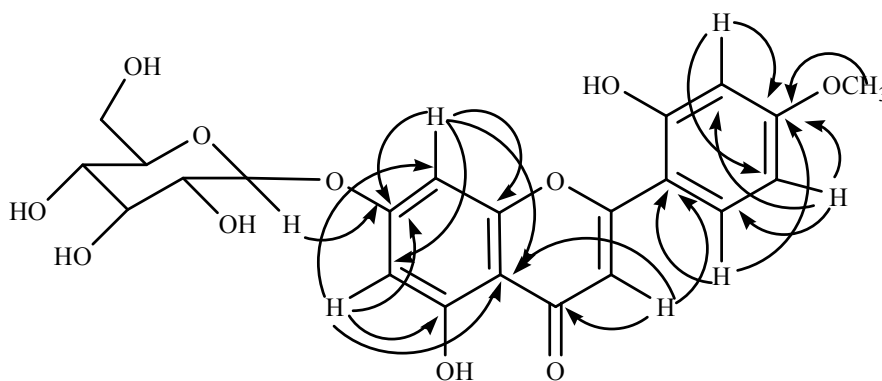
Compound **1** was isolated as yellow crystalline solid, m.p. 210-212 °C, deduced molecular formula C<sub>22</sub>H<sub>22</sub>O<sub>11</sub> from its FAB-MS. It gave positive Molisch test, Shinoda test and blue color with FeCl<sub>3</sub>, characteristic for flavone glycosides. The IR spectrum showed characteristic absorption bands for hydroxy (3350 cm<sup>-1</sup>) and carbonyl (1460 cm<sup>-1</sup>) functions. The <sup>1</sup>H NMR spectrum showed doublets at  $\delta$  6.46 ( $J = 1.8$  Hz, H-6) and  $\delta$  6.76 ( $J = 1.8$  Hz, H-8), indicating a tetrasubstituted aromatic ring. Other

doublets at  $\delta$  7.12 ( $J = 3.4$  Hz, H-3'), 6.92 ( $J = 8.4$  Hz, H-6') and 7.44 ( $J = 3.4, 8.4$  Hz, H-5') revealed the trisubstituted aromatic ring. The position of two singlets at  $\delta$  12.9 and 9.5 indicated two hydroxy groups, in which former is chelated with a carbonyl function and assigned at position OH-5. A sharp singlet at  $\delta$  3.61 correlated to C-4' ( $\delta$  145.81), indicating OCH<sub>3</sub>-4'. A doublet at  $\delta$  5.08 ( $J = 7.2$  Hz) indicated anomeric signal with other signals in the range of  $\delta$  3.2-4.6 for a  $\beta$  linked sugar. In the <sup>13</sup>C NMR spectrum, the downfield signal at  $\delta$  181.9 indicated a carbonyl group. The positions of substituted groups were confirmed by <sup>1</sup>H-<sup>13</sup>C correlation in HMBC (Figure 2) and HSQC. The correlation of H-3' ( $\delta$  7.12) to C-4' ( $\delta$  145.81) and C-5' ( $\delta$  116.02); H-5' ( $\delta$  7.44) to C-3' ( $\delta$  113.5), C-4' ( $\delta$  145.81) and C-6' ( $\delta$  119.21) and H-6' ( $\delta$  6.92) to C-1' ( $\delta$  121.42) and C-4' ( $\delta$  145.81) revealed the substitution at C-2' (OH) and C-4' in ring B. The correlation between the anomeric proton ( $\delta$  5.09) and C-7 ( $\delta$  162.98) indicated position of sugar at C-7. The sugar was identified as D-glucose by hydrolysis and direct comparison (co-PC) with authentic sugar. The chemical structure of compound 1 is given in Figure 1.

**Figure 1.** Chemical structure of compound 1.



**Figure 2.** Important HMBC correlations in compound 1.



### 3. Experimental Section

#### 3.1. General

Melting points were recorded on a Perfit melting point apparatus. UV spectra were measured on a Perkin-Elmer Lambda-25 spectrophotometer in methanol. IR spectra recorded on a Perkin-Elmer Spectrum RX1 FT-IR spectrometer (KBr discs). NMR spectra were obtained on Bruker Avance 300 and 500 spectrometers (300 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$ ,  $\text{CDCl}_3$  as solvent, TMS as internal standard). MS were recorded on Quattro II-EIMS and Jeol SX-102 (FAB) mass spectrometer. Column chromatography was performed on silica gel (Merck 60-120 mesh,  $15 \times 100$  cm). TLC was carried out on silica gel (Merck 10-40  $\mu$ ) precoated plates, spots were visualized by spraying with 7%  $\text{H}_2\text{SO}_4$ .

#### 3.2. Plant material

Aerial parts of *S. denticulata* were collected from Tungnath, Chamoli during the month of May and identified from Taxonomy Laboratory, Department of Botany, H.N.B. Garhwal University Srinagar. A voucher specimen (GUH-8036) of the plant has been kept in the Departmental Herbarium for future records.

#### 3.3. Extraction and isolation

The shade dried aerial parts of *S. denticulata* (6 kg) were powdered and extracted exhaustively with 95% ethanol (3 times) to yield a black brown extract, which was concentrated under reduced pressure and defatted with n-hexane. The extract (380 g) was pre-adsorbed with silica gel and applied on the top of a column prepared by silica gel (500 g) in  $\text{CHCl}_3$ . The elution was first started with  $\text{CHCl}_3$  and then  $\text{CHCl}_3$  with increasing amounts of MeOH (0-30%). Elution with  $\text{CHCl}_3$ :MeOH = 22:3 afforded compound **1**, whereas 9:1, 43:7, 41:9, 8:2 and 21:4 furnished  $\beta$ -sitosterol [8], 2,6-dihydroxy-4-methoxyacetophenone [9], eugenol-1-*O*- $\beta$ -D-glucopyranoside, 1-*O*- $\beta$ -D-(3'-benzoyl)-salicyl alcohol [10] and luteolin-7-*O*- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)-glucopyranoside [11,12], respectively.

#### 3.4. 5-Hydroxy-2-(2-hydroxy-4-methoxyphenyl)-4-oxo-4H-chromen-7-yl $\beta$ -D-glucopyranoside (**1**)

Yellow amorphous solid (60 mg); m.p. 210-212  $^\circ\text{C}$  (uncorr.); UV:  $\lambda_{\text{max}}^{\text{MeOH}}$ : 253, 278 and 353 nm; IR:  $\nu_{\text{max}}^{\text{KBr}}$ : 3373, 2907, 1703, 1293  $\text{cm}^{-1}$ ; NMR data: see Table 1; FAB-MS (m/z): 462  $[\text{M}]^+$ , 300  $[\text{M-glu}]^+$  149  $[\text{C}_9\text{H}_9\text{O}_2]^+$ ; calcd. C 57.14, H 4.80; found C 57.86, H 4.37.

**Table 1.**  $^{13}\text{C}$ ,  $^1\text{H}$ -NMR, HSQC and HMBC data of compound **1** in  $\text{CDCl}_3$ .

Position	$\delta_{\text{C}}$ ppm	$\delta_{\text{H}}$ ppm (J Hz)	HSQC	HMBC
2	161.16	-	-C-	-
3	103.20	6.79, s	-CH-	4, 4a, 1'
4	181.93	-	-C-	-
4a	105.37	-	-C-	-
5	164.50	-	-C-	-
6	99.57	6.46 (d, 1.8)	-CH-	4a, 5, 7, 8
7	162.98	-	-C-	-
8	97.76	6.76 (d, 1.8)	-CH-	6, 7, 4a, 8a
8a	156.98	-	-C-	-
1'	121.42	-	-C-	-
2'	149.95	-	-C-	-
3'	113.59	7.12 (d, 3.4)	-CH-	4', 5'
4'	145.81	-	-C-	-
5'	116.02	7.44 (dd, 3.4, 8.4)	-CH-	1', 3', 4', 6'
6'	119.21	6.92 (d, 8.4)	-CH-	1', 2', 4', 5'
1''	99.92	5.09 (d, 7.2)	-CH-	7
2''	70.36	3.29 (d, 8.8)	-C-	-
3''	73.15	3.34 (t, 8.8)	-CH-	-
4''	76.42	3.32, m	-CH-	-
5''	77.19	3.49, m	-CH-	-
6''	60.65	3.73, m	-CH <sub>2</sub> -	-
OCH <sub>3</sub> -4'	55.82	3.61, s	-CH <sub>3</sub>	4'
OH-5	-	12.9	-	-
OH-2'	-	9.5	-	-

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