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## Note

### A novel cyanogenic glycoside from *Semiaquilegia adoxoides*

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Phytochemical investigation of *Semiaquilegia adoxoides* was initiated in view of its common usage in traditional Chinese medicine and the scarcity of previous phytochemical studies. Fractionation of an ethanol extract from the roots of this plant led to the isolation and identification of a novel cyanogenic glycoside, 2-( $\beta$ -D-glucopyranosyloxy)-4-hydroxybenzeneacetonitrile (**1**). The structure of **1** was elucidated on the basis of IR, FAB-MS, 1D and 2D NMR spectral analysis.

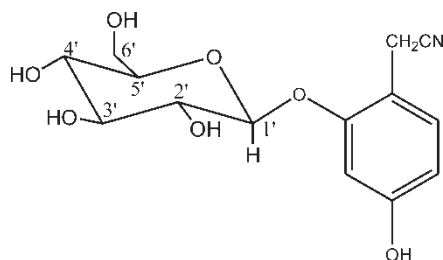
**Keywords:** 2-( $\beta$ -D-Glucopyranosyloxy)-4-hydroxybenzeneacetonitrile; *Semiaquilegia adoxoides*; Cyanogenic glycoside

## 1. Introduction

The naturally occurring cyanogenic glycosides are present in more than 2500 plant species and have been demonstrated to have a relatively broad distribution in the following plant families: Ranunculaceae, Rosaceae, Linaceae, Caprifoliaceae, Compositae, Poaceae, and Euphorbiaceae. Most identified cyanogenic glycosides are those of  $\alpha$ -hydroxynitrile and  $\beta$ -linked with D-glucose. To the best of our knowledge, there are few examples of  $\gamma$ -hydroxynitrile glycosides reported in natural product research, with the aglycones of aliphatic groups [1,2].

The roots of *Semiaquilegia adoxoides* (DC.) Makino (Ranunculaceae) (Chinese name “Tian-Kui-Zi”) are reported in Chinese Pharmacopoeia as a traditional Chinese medicine for several symptoms. The roots have often been used to treat tonsillitis, mastitis, scrofula, and cancer since they are believed to possess antibacterial, anti-inflammatory and antineoplastic activities [3]. However, phytochemical studies have been rarely conducted on *Semiaquilegia* probably due to the fact that it consists of only one member. Moreover, only six known compounds, including  $\beta$ -sitosterol, diosgenin, griffonilide, lithospermoside, magnoflorine, and one flavonoid glycoside, semiaquilinoside, were identified from the roots and aerial parts of the title plant [4,5]. In our search for new glycosides and related-derivatives we

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Figure 1. Structure of compound **1**.

investigated the chemical constituents of the roots of *Semiaquilegia adoxoides* and isolated a novel cyanogenic glycoside, 2-(β-D-glucopyranosyloxy)-4-hydroxybenzeneacetonitrile (**1**, figure 1). Here we report the elucidation of its structure on the basis of IR, FAB-MS,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, DEPT, HMQC, and HMBC spectral analysis.

## 2. Results and discussion

Compound **1** was obtained as white needles. Its FAB-MS spectrum under positive ion mode gave a quasi-molecular ion at  $m/z$  312 and another ion at  $m/z$  149 corresponding to  $[\text{C}_{14}\text{H}_{17}\text{O}_7\text{N} + \text{H}]^+$  and  $[\text{C}_{14}\text{H}_{17}\text{O}_7\text{N} - 162]^+$ , indicating a nitrogen atom and a hexose sugar moiety in the molecule. A strong  $[\text{M} + \text{H}]^+$  ion peak at  $m/z$  312.1090 (calculated for  $\text{C}_{14}\text{H}_{18}\text{O}_7\text{N}$ , 312.1083) in the high-resolution FAB-MS spectrum of **1** confirmed the above deduction. The IR spectrum of **1** showed absorption bands at 3312 (OH) and  $2262\text{ cm}^{-1}$  (CN); the latter is characteristic of the triple-bond stretching vibrations of a nitrile group. A survey of the  $^1\text{H}$  NMR spectrum of **1** revealed proton signals typical (7.14, d,  $J = 8.1$  Hz; 6.48, dd,  $J = 8.1, 2.4$  Hz; 6.69, d,  $J = 2.4$  Hz) of a trisubstituted aromatic ring (AMX spin system). Of the fourteen carbon signals in the  $^{13}\text{C}$  NMR spectrum of **1**, six were assigned to the hexopyranose ring (glucopyranose in β-D form was deduced from the anomeric proton signal at 4.85, d,  $J = 6.9$  Hz), and the remaining eight to the benzeneacetonitrile fragment. The positions of three benzene substitutions and the full assignments of the NMR signals for compound **1** were established by studies of the related spectra (DEPT, HMQC, and HMBC) and by comparison with literature data [2,6] (figure 2 and table 1). Based on the above-mentioned analysis, the structure of compound **1** was determined as 2-(β-D-glucopyranosyloxy)-4-hydroxybenzeneacetonitrile.

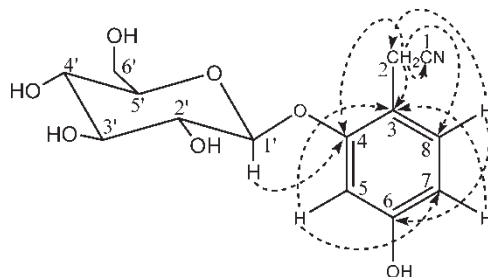
Figure 2. Key HMBC correlations of **1**.

Table 1.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of **1** in  $\text{CD}_3\text{OD}$ .

No.	$\delta_{\text{C}}$ (ppm)	Carbon unit	$\delta_{\text{H}}$ (ppm) with multiplicities and $J$
1	120.1	C	–
2	18.1	$\text{CH}_2$	3.78, s
3	112.3	C	–
4	157.3	C	–
5	104.5	CH	6.69, d, $J = 2.4$ Hz
6	159.9	C	–
7	110.6	CH	6.48, dd, $J = 8.1, 2.4$ Hz
8	130.7	CH	7.14, d, $J = 8.1$ Hz
1'	103.0	CH	4.85, d, $J = 6.9$ Hz
2'	74.8	CH	ca. 3.42, overlapped
3'	78.0	CH	ca. 3.47, overlapped
4'	71.8	CH	ca. 3.48, overlapped
5'	78.2	CH	ca. 3.42, overlapped
6'	62.3	$\text{CH}_2$	3.90, br d, $J = 12.0$ Hz 3.71, dd, $J = 12.0, 3.6$ Hz

### 3. Experimental

#### 3.1 General experimental procedures

The melting point was determined on a XT4A micro-melting point apparatus and is uncorrected. Optical rotation was measured on a Perkin-Elmer 241 polarimeter. The IR spectrum was recorded with a Hitachi 270-30 infrared spectrometer. NMR spectra were recorded in  $\text{CD}_3\text{OD}$  on a Varian Mercury-300 MHz spectrometer. The FAB mass spectrum was obtained on a VG ZAB-HZ mass spectrometer, and high-resolution FAB-MS on an Autospec-UltimaETOF mass spectrometer. Silica gel (100–200 mesh, 200–300 mesh and GF<sub>254</sub> Type 60, Qingdao Marine Chemical Co.) was used for open-column chromatography and TLC. Spots were visualized on TLC by heating after spraying with 5%  $\text{H}_2\text{SO}_4$  in EtOH.

#### 3.2 Plant material

The roots of *Semiaquilegia adoxoides* (DC.) Makino (Ranunculaceae) were collected in Chaohu, Anhui Province, China during the early summer of 2001 and identified by one of the authors (Y.F. Su). A voucher specimen has been deposited in the Natural Product Chemistry Laboratory, the College of Pharmaceuticals and Biotechnology, Tianjin University.

#### 3.3 Extraction and isolation

Concentration of the 95% ethanol extract of the roots of *S. adoxoides* (19.7 kg) and re-extraction of the water suspension with light petroleum (60–90°C), chloroform, ethyl acetate and n-butanol in turn yielded 926 g of a butanol extract, which was then exposed to a D101 macroporous resin column, eluting gradiently with ethanol in water ( $\text{H}_2\text{O}$ , 30% EtOH, 50% EtOH, 70% EtOH, and EtOH). The 30% aqueous ethanol eluate (60 g) was subjected to silica-gel column chromatography. Gradient elution with chloroform-methanol ( $\text{CHCl}_3$ : MeOH, 8.5:1.5, 8:2, 7.5:2.5, 7:3, 4000 ml for each gradient) gave 38 fractions. Fraction 16 was subjected to open-silica gel column, eluting with  $\text{H}_2\text{O}$ -saturated ethyl acetate, to furnish **1** (12 mg).

Compound **1** was obtained as white needles from MeOH, mp 201–202°C,  $[\alpha]_D^{28} -78.5^\circ$  (*c* 0.6, MeOH); IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3312 (OH), 2964, 2262 (CN), 1618, 1517, 1293, 1077, 1027, 839; For <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) and <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) data see Table I; FAB-MS *m/z* 312 [M + H]<sup>+</sup>, 149 [M - 162]<sup>+</sup>, HR FAB-MS *m/z* 312.1090 [M+H]<sup>+</sup>.

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