

A New Disaccharide from the Fern *Macrothelypteris digophlebia*

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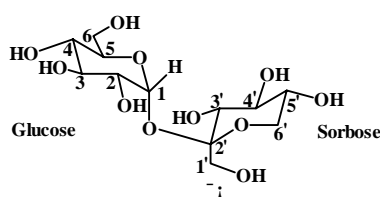
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Abstract: A new disaccharide, digobiose **1**, was isolated from the rhizomes of *Macrothelypteris digophlebia* (Bak.) Ching var. *elegans* (koidz.). Its structure which is very similar with that of sucrose was identified as α -D-glucopyranosyl (1 \rightarrow 2')- β -D-sorbopyranoside by spectroscopic analysis.

Keywords: *Macrothelypteris digophlebia*, disaccharide, digobiose.

In continuation of our search for plant-derived bioactive principles, we investigated the chemical constituents of *Macrothelypteris digophlebia* (Bak.) Ching var. *elegans* (koidz.) (Thelypteridaceae) collected at QinLing Mountain region of Shaanxi Province¹. The present paper deals with herein the structural elucidation of a rare new biose **1**, named digobiose, isolated from the EtOH extract of the rhizomes of this plant.

Figure 1. The structure of digobiose **1**



Compound **1** (0.015 %), colorless crystals, m.p.180 °C, $[\alpha]_D^{23} + 68.59$ (c 0.00554, H₂O). It exhibited a molecular ion peak at m/z 341[M-1]⁻ in FABMS. The molecular formula of **1** was determined to be C₁₂H₂₂O₁₁ by the negative ion HRFAB-MS ([M-H]⁻ 341.112637, calcd.341.108387) and, ¹H and ¹³C NMR spectral data. Its IR spectrum revealed the strong absorption of hydroxyls at 3000–3564, and ether bonds at 1129,1070,1052,1007 cm⁻¹. On acid hydrolysis, **1** gave D-glucose and D-sorbose detected by comparison with authentic samples on TLC. Twelve carbon signals in the range δ 60–110 ppm in the ¹³C NMR (DEPT) spectrum of **1** further suggested that **1** is a biose composed of two six-carbon sugar moieties. Those were recognized as 1×C,8×CH,3×CH₂ (**Table 1**), in which two anomeric carbons at δ 94.95 and 106.42, and the latter assigned as one quaternary carbon of the sorbose, and three oxymethylene at δ

62.87, 64.09 and 65.09 attributed to glu C-6, sor C-1' and C-6', respectively, were given. Its ^1H NMR spectrum showed the presence of one anomeric proton signal at δ 5.362 (1H, d, 3.9 Hz), attached to the anomeric carbon of glu C-1 at δ 94.95, which confirmed that the glucose had α glycosidic linkage. In addition, the hydroxymethyl group at C-2' is in axial orientation², because the conformation of the sorbose is more stable, and the other linkage should be determined to be β form. The assignments of both protons and carbons in **1** were made by means of ^1H - ^1H COSY, ^1H - ^{13}C COSY, and COLOC spectra. Thus, the above evidence led to the establishment of the structure of **1** as α -D-glucopyranosyl (1 \rightarrow 2')- β -D-sorbopyranoside (**Figure 1**).

Table 1. 1D and 2DNMR spectral data for **1** (400 / 500 MHz, D₂O,)

| | C | DEPT | H | |
|------------|----------|-----------------|-------|-------------------------|
| Glucose-1 | 94.95 d | CH | 5.362 | 1H, d, J = 3.9 Hz |
| 2 | 73.78 d | CH | 3.507 | 1H, dd, J = 3.9, 9.9 Hz |
| 3 | 75.20 d | CH | 3.710 | 1H, dd, J = 9.5, 9.5 Hz |
| 4 | 71.94 d | CH | 3.421 | 1H, dd, J = 9.4, 9.4 Hz |
| 5 | 75.17 d | CH | 3.771 | 1H, m |
| 6 | 62.87 t | CH ₂ | 3.800 | 2H, m |
| Sorbose-1' | 64.09 t | CH ₂ | 3.621 | 2H, br s |
| 2' | 106.42 d | C | | |
| 3' | 78.96 d | CH | 4.171 | 1H, d, J = 8.8 Hz |
| 4' | 76.96 d | CH | 4.002 | 1H, dd, J = 8.6, 8.8 Hz |
| 5' | 74.90 d | CH | 3.854 | 1H, m |
| 6' | 65.09 t | CH ₂ | 3.771 | 2H, m |

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