

Communication

## New Flavonolignan Glycosides from the Aerial Parts of *Zizania latifolia*

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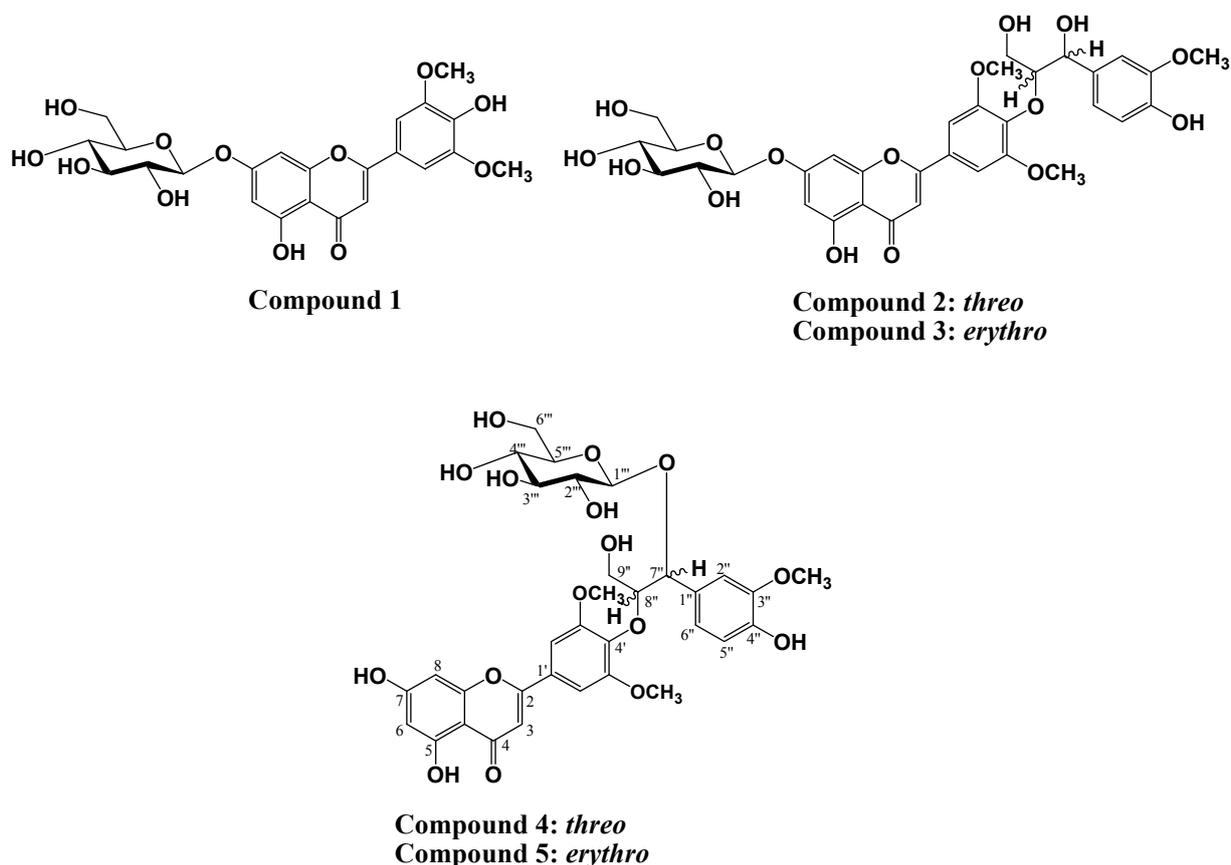
**Abstract:** Two new flavonolignan glycosides, tricin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose (**4**) and tricin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose (**5**) were isolated from the roots of *Zizania latifolia*, together with tricin-7-*O*- $\beta$ -D-glucopyranose (**1**), tricin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7-*O*- $\beta$ -D-glucopyranose (**2**), and tricin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7-*O*- $\beta$ -D-glucopyranose (**3**). Their structures were identified on the basis of spectroscopic techniques, including HR-ESI/MS, 1D-NMR (<sup>1</sup>H, <sup>13</sup>C, DEPT), 2D-NMR (gCOSY, gHSQC, gHMBC), and IR spectroscopy.

**Keywords:** *Zizania latifolia*; flavonolignan glycoside; tricin-7-*O*- $\beta$ -D-glucopyranose

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## 1. Introduction

*Zizania latifolia* Turcz (wild rice) is cultivated in various regions of Southeastern Asia, including Korea, Japan, and China. Particularly, in China, wild rice grain is used as an important traditional medicine to treat anemia and fever in addition to heart, kidney, and liver disorders. It has been reported that wild rice species possess rich nutrient content [1,2], as well as diverse biological activities such as anti-obesity [3], anti-oxidant [4], anti-inflammatory and anti-allergenic effects [5]. Previous phytochemical studies on *Z. latifolia* have confirmed the presence of flavonolignan groups along with triclin. In order to identify phytochemical components of *Z. latifolia*, isolation and structural determination of two new flavonolignan glycosides, triclin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose (**4**) and triclin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose (**5**), a flavone glycoside, triclin-7-*O*- $\beta$ -D-glucopyranose (**1**), two known flavonolignan glycosides triclin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7-*O*- $\beta$ -D-glucopyranose (**2**), and triclin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7-*O*- $\beta$ -D-glucopyranose (**3**) were performed. These compounds are of particular interest since flavonolignan glycosides have been reported for the first time from *Z. latifolia* (Figure 1).



**Figure 1.** Chemical structures of isolated compounds 1–5.

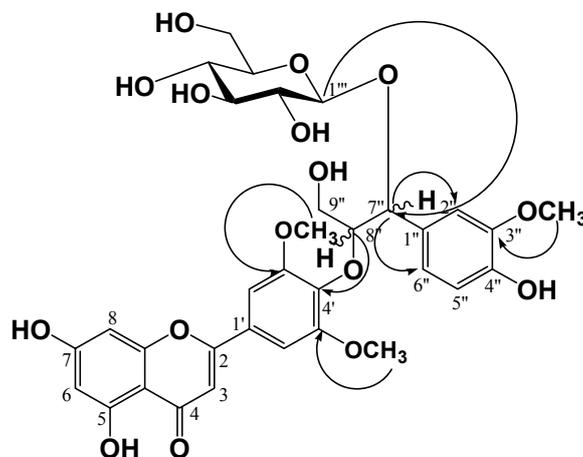
## 2. Results and Discussion

The aerial parts were extracted using 80% MeOH, and the concentrated extracts were successively partitioned using EtOAc, n-BuOH, and H<sub>2</sub>O. Repeated SiO<sub>2</sub>, and ODS-A column chromatographic separation of the EtOAc fraction produced a purified flavone glycoside, and four flavonolignans

including two new flavonolignan glycosides. These compounds were identified as tricetin-7-*O*- $\beta$ -D-glucopyranose (**1**), tricetin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7-*O*- $\beta$ -D-glucopyranose (**2**), tricetin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7-*O*- $\beta$ -D-glucopyranose (**3**), tricetin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose (**4**) and tricetin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose (**5**), respectively, based on interpretation of the spectroscopic data including NMR, MS, and IR spectroscopy, and confirmed by comparison of the data with those reported in the literature [6–8]. All compounds were isolated for the first time from *Z. latifolia*.

Compound **4** (a yellow amorphous powder) was developed by TLC, followed by spraying with 10% H<sub>2</sub>SO<sub>4</sub> and heating to produce a dark yellow color. In the <sup>1</sup>H-NMR spectrum, three olefin methine proton signals at  $\delta$  7.50 (1H, d,  $J$  = 1.6 Hz, H-2''), 7.37 (1H, dd,  $J$  = 8.0, 1.6 Hz, H-6''), and 7.18 (1H, d,  $J$  = 8.0 Hz, H-5'') were observed due to a 1,2,4-trisubstituted benzene ring along with five olefin methine proton signals at  $\delta$  7.27 (2H, br. s, H-2', 6'), 6.97 (1H, s, H-3), 6.83 (1H, d,  $J$  = 2.0 Hz, H-8), and 6.72 (1H, d,  $J$  = 2.0 Hz, H-6) due to a flavone moiety. In the oxygenated region, two oxygenated methylene proton signals at  $\delta$  5.89 (1H, d,  $J$  = 6.0 Hz, H-7'') and 5.19 (1H, m, H-8''), an oxygenated methylene proton signal at  $\delta$  4.75 (1H, dd,  $J$  = 12.4, 3.6 Hz, H-9''a) and 4.36 (1H, dd,  $J$  = 12.0, 2.8 Hz, H-9''b), and three methoxy proton signals at  $\delta$  3.81 (6H, s, H-3', 5'-OCH<sub>3</sub>) and 3.74 (3H, s, H-3''-OCH<sub>3</sub>) were observed. There were also oxygenated methine and methylene signals for a monosaccharide moiety observed in the region from  $\delta$  4.12 to 4.28, including one hemiacetal proton signal at  $\delta$  5.54 (1H, d,  $J$  = 8.0 Hz, H-1'') with a <sup>3</sup> $J_{\text{H}1''/\text{H}2''}$  coupling constant of 8.0 Hz, indicating an anomer hydroxy in  $\beta$ -configuration. The relative configuration of chiral carbons, C-7'' and C-8'', in compound (**4**) was deduced to be *threo* type from the coupling constant ( $J$  = 6.0 Hz) between the oxygenated methine signals H-7'' ( $\delta_{\text{H}}$  5.89) and H-8'' ( $\delta_{\text{H}}$  5.19). It was reported that the  $J_{\text{H}-7'',8''}$  coupling constant of proton resonance in the guaiacylglyceryl moiety can be used to distinguish between the *erythro* and *threo* forms, with  $J$  values of 4.0–5.0 and 6.0–7.0 Hz, respectively [9–11]. The <sup>13</sup>C-NMR spectrum showed 33 carbon signals including three methoxy carbons [ $\delta$  52.3 (C-3', 5'-OCH<sub>3</sub>) and 56.6 (C-3''-OCH<sub>3</sub>)], confirming that compound **4** was a flavonoid with a phenylpropanoid moiety and hexose moiety. In the low-magnetic field region, a conjugated ketone carbon  $\delta$  183.9 (C-4), seven oxygenated olefin quaternary carbons [ $\delta$  167.3 (C-7), 165.0 (C-2), 164.3 (C-5), 159.7 (C-9), 155.1 (C-3', 5'), 141.3 (C-4')], two olefin quaternary carbons [ $\delta$  127.9 (C-1'), 106.3 (C-10)], and five olefin methine carbons [ $\delta$  107.0 (C-3), 105.9 (C-2', 6'), 101.3 (C-6), 96.3 (C-8)] signals were observed, indicating the presence of a flavone moiety. In addition, two oxygenated olefin quaternary carbons [ $\delta$  149.8 (C-3''), 149.1 (C-4'')], one olefin quaternary carbon  $\delta$  133.1 (C-1''), and three olefin methine carbons [ $\delta$  122.8 (C-6''), 117.0 (C-5''), 114.0 (C-2'')], two oxygenated methine carbons [ $\delta$  87.8 (C-8''), 82.6 (C-7'')] and one oxygenated methylene carbon  $\delta$  62.7 (C-9'') signals were observed, indicating the presence of a phenylpropanoid moiety. In the HMBC spectrum, the oxygenated methine proton  $\delta_{\text{H}}$  5.19 (1H, m, H-8'') showed a correlated cross peak with an oxygenated olefin quaternary carbon  $\delta_{\text{C}}$  141.3 (C-4'), indicating that the flavone and phenylpropanoid moieties were linked between  $\delta_{\text{C}}$  C-8'' and  $\delta_{\text{C}}$  C-4' via an ether linkage, as well as a cross-peak between an anomer proton signal at  $\delta_{\text{H}}$  5.54 (1H, d,  $J$  = 8.0 Hz, H-1'') and an oxygenated methine carbon signal at  $\delta_{\text{C}}$  82.6 (C-7''), indicating that glucose was attached to the C-7'' of the phenylpropanoid through a glycosidic linkage (Figure 2). Finally, the structure of compound (**4**) was determined to be tricetin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose, which is salcolin A 7''-*O*- $\beta$ -D-glucopyranose. The molecular weight was determined to be

688.2003 from the pseudomolecular ion peak at  $m/z$  687.1962  $[M-H]^-$  in the negative high resolution ESI-MS (calculated for  $C_{33}H_{35}O_{16}$ ).



**Figure 2.** Key HMBC correlations of compound 4.

Signals in the  $^1H$ -NMR (400 MHz, pyridine- $d_5$ ,  $\delta_H$ ) and  $^{13}C$ -NMR (100 MHz, pyridine- $d_5$ ,  $\delta_C$ ) spectra of compound 5 were almost the same as those of compound 4, with the exception of the relative stereostructure of C-7'' and C-8''. Compound 5 was confirmed to be *erythro* type from the coupling constant between the oxygenated methine signals of H-7'' and H-8'' ( $J = 4.8$  Hz). The ether linkage (C-8''/C-4') and glycosidic linkage (C-1''/C-7'') were confirmed from the cross peak between the oxygenated methine proton  $\delta_H$  5.16 (1H, m, H-8'') and oxygenated olefine quaternary carbon  $\delta_C$  142.0 (C-4'), as well as the cross-peak between the anomer proton signal at  $\delta_H$  5.35 (1H, d,  $J = 8.0$  Hz, H-1'') and a oxygenated methine carbon signal at  $\delta_C$  81.9 (C-7'') in the HMBC spectrum. Consequently, the structure of compound 5 was determined to be tricin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose, which is salcolin B 7''-*O*- $\beta$ -D-glucopyranose. The molecular weight was determined to be 688.2003 from the pseudomolecular ion peak at  $m/z$  687.1952  $[M-H]^-$  in the negative high resolution ESI-MS (calculated for  $C_{33}H_{35}O_{16}$ ).

### 3. Experimental

#### 3.1. General

Preparative-liquid chromatography (prep-LC) (LC-Forte/R, YMC, Kyoto, Japan) was carried out using cartridge YMC-DispoPack (ODS-25, 80 g, and 120 g, YMC). Silica gel (230–400 mesh, Merck, Darmstadt, Germany) and Sephadex LH-20 (Merck) were used for column chromatography. Thin-layer Chromatography (TLC) analysis was performed using on a Kiesel gel 60F<sub>254</sub> plate (Merck) and a RP-18 F<sub>254s</sub> plates (Merck), and detection was performed by a UV lamp at 254 and 365 nm and 10%  $H_2SO_4$  solution by spraying and heating.  $^1H$  and  $^{13}C$ -NMR along with 2D-NMR data were obtained on a Bruker AVANCE II 400 ( $^1H$ -NMR at 400 MHz,  $^{13}C$ -NMR at 100 MHz) spectrometer (Bruker, Rheinstetten, Germany) in pyridine- $d_5$  with TMS as internal standard. ESI/MS was obtained on a AB SCIEX triple TOF 5600 mass spectrometer (AB SCIEX, Concord, ON, Canada). All the reagent grade chemicals were purchased from Sigma Chemical Co. (St. Louis, MO, USA).

### 3.2. Plant Material

*Plant sample.* Dried aerial parts of *Z. latifolia* was purchased from store located at Yeongcheon City, Gyeongbuk, Korea. A voucher specimen (KHU-0130301) was deposited at the Laboratory of Natural Products Chemistry, Kyung Hee University, Yongin, Korea.

### 3.3. Extraction and Isolation

Dried powder (5 kg) was extracted at room temperature with 80% MeOH (45 L). The concentrated extract was partitioned with water (3 L), EtOAc (3 L) and n-BuOH (3 L) successively to produce. EtOAc extract (97 g, ZLE), n-BuOH extract (240 g, ZLB) and H<sub>2</sub>O extract (57 g, ZLW). The EtOAc extract was applied to a silica gel c.c. (12 × 14 cm), and eluted with CHCl<sub>3</sub> : MeOH (50:1 → 30:1 → 20:1 → 12:1 → 10:1 → 7:1 → 5:1 → 3:1 → 1:1, each 3 L) monitoring by thin layer chromatography (TLC) to produce 13 fractions (ZLE-1 to ZLE-13). Fraction ZLE-12 (5.0 g) was combined and subjected to MPLC column chromatography: YMC-DispoPack AT (ODS-25:120 g, particle size: 25 μm). The fractions were analyzed by a UV detector at 254 and 356 nm, and the mobile phase consisted of A: 0.1% formic acid in water, B: 0.1% formic acid in acetonitrile with a flow rate of 10 mL/min. The gradient consisted of 10% B held for 20 min to 30% B at a rate of 0.25%/min, from 30% B to 50% B at a rate of 0.20%/min, from 50% B to 70% B at a rate of 0.25%/min, and from 70% B to 90% B at a rate of 0.30%/min. A total 11 fractions (ZLE-12-1 to ZLE-12-15) were obtained. ZLE-12-10 (642 mg) was subjected to MPLC column chromatography: YMC-DispoPack AT (ODS-25: 80 g, particle size: 25 μm), with A: 0.1% formic acid in water, B: 0.1% formic acid in acetonitrile as the mobile phase at a flow rate of 5 mL/min. The detector was maintained at 254 and 356 nm. The gradient consisted of 20% B to 50% B at a rate of 0.5%/min, and 50% B to 70% B at a rate of 0.6%/min. Compound **1** (32 mg, RT = 6.05 min), compound **2** (35 mg, RT = 7.8 min), compound **3** (42 mg, RT = 9.2 min), compound **4** (22 mg, RT = 12.4 min) and compound **5** (31 mg, RT = 14.6 min) were obtained.

### 3.4. Spectroscopic Data

*Tricin-7-O-β-D-glucopyranose (1).* Pale yellow powder (CH<sub>3</sub>OH); negative ESI/MS *m/z* 491 [M-H]<sup>-</sup>; IR (KBr) 3380, 2921, 1730, 1652, 1613, 1491, 1358, 1084 cm<sup>-1</sup>; <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>) δ 7.55 (2H, s, H-2', 6'), 7.17 (1H, d, *J* = 2.0 Hz, H-8), 7.02 (1H, s, H-3), 6.86 (1H, d, *J* = 2.0 Hz, H-6), 5.78 (1H, d, *J* = 7.2 Hz, H-1''), 4.55 (1H, dd, *J* = 10.4, 1.2 Hz, H-6'''a), 4.38-4.10 (5H, m, H-2''', H-3''', H-4''', H-5''', 6'''b-OCH<sub>2</sub>), 3.87 (6H, s, OCH<sub>3</sub>-3', 5'). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>) δ 182.8 (C-4), 164.9 (C-2), 164.0 (C-7), 162.5 (C-5), 157.8 (C-9), 149.5 (C-3', 5'), 142.2 (C-4'), 121.0 (C-1'), 106.5 (C-10), 105.1 (C-2', 6'), 104.5 (C-3), 101.7 (C-1''), 100.6 (C-6), 95.5 (C-8), 79.2 (C-3'''), 78.4 (C-5'''), 74.7 (C-2''), 71.0 (C-4''), 62.2 (C-6''), 56.5 (C-3', 5'-OCH<sub>3</sub>).

*Tricin-4'-O-(threo-β-guaiacylglyceryl) ether 7-O-β-D-glucopyranose (2).* Yellow amorphous powder (CH<sub>3</sub>OH); Negative ESI/MS *m/z* 687 [M-H]<sup>-</sup>; IR (KBr) 3369, 2938, 1652, 1611, 1588, 1512, 1495, 1356, 1263, 1159, 1124, 841 cm<sup>-1</sup>; <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>) δ 7.53 (1H, s, H-2''), 7.37 (1H, dd, *J* = 8.0, 1.6 Hz, H-6''), 7.31 (2H, s, H-2', 6'), 7.26 (1H, d, *J* = 8.0 Hz, H-5''), 7.14 (1H, d, *J* = 2.4 Hz,

H-8), 7.01 (1H, s, H-3), 6.85 (1H, d,  $J = 2.0$  Hz, H-6), 5.76 (1H, d,  $J = 7.2$  Hz, H-1'''), 5.70 (1H, d,  $J = 5.2$  Hz, H-7''), 5.08 (1H, q,  $J = 5.2, 3.2$  Hz, H-8''), 4.65 (1H, dd,  $J = 12.0, 5.2$  Hz, H-9''e), 4.54 (1H, dd,  $J = 12.0, 2.4$  Hz, H-6'''a), 4.28 (1H, m, H-9''a), 4.36-4.27 (5H, m, H-2''', H-3''', H-4''', H-5''', 6'''b-OCH<sub>2</sub>), 3.84 (6H, s, OCH<sub>3</sub>-3', 5'), 3.74 (3H, s, OCH<sub>3</sub>-3''). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>)  $\delta$  184.1 (C-4), 165.5 (C-7), 165.4 (C-2), 163.7 (C-5), 159.1 (C-9), 155.3 (C-3', 5'), 149.6 (C-3''), 148.6 (C-4''), 141.9 (C-4'), 135.6 (C-1''), 127.7 (C-1'), 121.8 (C-6''), 117.3 (C-5''), 112.9 (C-2''), 107.8 (C-10), 107.1 (C-3), 106.1 (C-2', 6'), 103.0 (C-1'''), 102.1 (C-6), 96.8 (C-8), 89.4 (C-8''), 80.5 (C-3'''), 79.7 (C-5'''), 76.0 (C-4'''), 75.1 (C-7''), 72.4 (C-2''), 63.5 (C-6'''), 62.9 (C-9''), 57.7 (C-3', 5'-OCH<sub>3</sub>), 57.1 (C-3''-OCH<sub>3</sub>).

*Tricin-4'-O-(erythro- $\beta$ -guaiacylglyceryl) ether 7-O- $\beta$ -D-glucopyranose (3)*. Yellow amorphous powder (CH<sub>3</sub>OH); Negative ESI/MS  $m/z$  687 [M-H]<sup>-</sup>; IR (KBr) 3364, 2933, 1649, 1607, 1590, 1495, 1457, 1358, 1121, 832 cm<sup>-1</sup>; <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>)  $\delta$  7.57 (1H, s, H-2''), 7.46 (1H, dd,  $J = 8.0, 1.2$  Hz, H-6''), 7.29 (2H, s, H-2', 6'), 7.26 (1H, d,  $J = 8.0$  Hz, H-5''), 7.13 (1H, d,  $J = 2.0$  Hz, H-8), 6.99 (1H, s, H-3), 6.86 (1H, d,  $J = 2.0$  Hz, H-6), 5.77 (1H, d,  $J = 6.0$  Hz, H-7''), 5.76 (1H, d,  $J = 7.2$  Hz, H-1'''), 4.95 (1H, q, H-8''), 4.54 (1H, br. d,  $J = 10.4$  Hz, H-6'''a), 4.43 (1H, dd,  $J = 11.6, 4.0$  Hz, H-9''a), 4.37-4.10 (5H, m, H-2''', H-3''', H-4''', H-5''', 6'''b-OCH<sub>2</sub>), 4.06 (1H, dd,  $J = 12.0, 4.0$  Hz, H-9''b), 3.82 (6H, s, OCH<sub>3</sub>-3', 5'), 3.77 (3H, s, OCH<sub>3</sub>-3''). <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>)  $\delta$  183.5 (C-4), 165.0 (C-7), 164.9 (C-2), 163.3 (C-5), 158.6 (C-9), 154.6 (C-3', 5'), 149.1 (C-3''), 148.2 (C-4''), 141.9 (C-4'), 134.6 (C-1''), 127.2 (C-1'), 121.4 (C-6''), 116.8 (C-5''), 112.6 (C-2''), 107.4 (C-3), 106.6 (C-10), 105.9 (C-2', 6'), 105.7 (C-1'''), 101.3 (C-6), 96.3 (C-8), 87.8 (C-8''), 80.0 (C-3'''), 79.2 (C-5'''), 75.5 (C-4'''), 74.4 (C-7''), 71.9 (C-2''), 63.9 (C-6'''), 62.5 (C-9''), 57.6 (C-3', 5'-OCH<sub>3</sub>), 57.1 (C-3''-OCH<sub>3</sub>).

*Tricin-4'-O-(threo- $\beta$ -guaiacylglyceryl) ether 7''-O- $\beta$ -D-glucopyranose (4)*. Yellow amorphous powder (CH<sub>3</sub>OH); HRESI/MS  $m/z$  687.1962 [M-H]<sup>-</sup>; IR (KBr) 3406, 1639, 1614, 1495, 1358, 1121 cm<sup>-1</sup>; <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>) and <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>), see Table 1.

*Tricin-4'-O-(erythro- $\beta$ -guaiacylglyceryl) ether 7''-O- $\beta$ -D-glucopyranose (5)*. Yellow amorphous powder (CH<sub>3</sub>OH); HRESI/MS  $m/z$  687.1952 [M-H]<sup>-</sup>; IR (KBr) 3432, 2502, 1685, 1510, 1420, 1399, 1112 cm<sup>-1</sup>; <sup>1</sup>H-NMR (pyridine-*d*<sub>5</sub>) and <sup>13</sup>C-NMR (pyridine-*d*<sub>5</sub>), see Table 1.

**Table 1.** <sup>1</sup>H- (400 MHz) and <sup>13</sup>C-NMR (100 MHz) data of compound 4–5 (in pyridine-*d*<sub>5</sub>,  $\delta$  in ppm,  $J$  in Hz).

No.	Compound 4		Compound 5	
	$\delta_C$	$\delta_H$ , Coupling Pattern, $J$ in Hz	$\delta_C$	$\delta_H$ , Coupling Pattern, $J$ in Hz
2	165.0		165.2	
3	107.0	6.97, s	107.2	7.00, s
4	183.9		183.9	
5	164.3		164.4	
6	101.3	6.72, d, 2.0	101.4	6.74, d, 2.0
7	167.3		167.3	
8	96.3	6.83, d, 2.0	96.3	6.86, d, 2.0
9	159.7		159.8	
10	106.3		106.3	

Table 1. Cont.

No.	Compound 4		Compound 5	
	$\delta_C$	$\delta_H$ , Coupling Pattern, $J$ in Hz	$\delta_C$	$\delta_H$ , Coupling Pattern, $J$ in Hz
1'	127.9		128.2	
2'	105.9	7.27, br. s	106.0	7.29, br. s
3'	155.1		155.1	
4'	141.3		142.0	
5'	155.1		155.1	
6'	105.9	7.27, br. s	106.0	7.29, br. s
1''	133.1		132.1	
2''	114.0	7.50, d, 1.6	113.9	7.59, d, 1.6
3''	149.4		149.4	
4''	148.8		148.9	
5''	117.0	7.18, d, 8.0	117.1	7.21, d, 8.0
6''	122.8	7.37, dd, 8.0, 1.6	122.5	7.43, dd, 8.0, 1.6
7''	82.6	5.89, d, 6.0	81.9	6.02, d, 4.8
8''	87.8	5.19, m	87.6	5.16, m
9''a	62.7	4.75, dd, 12.4, 3.6	63.0	4.44, dd, 12.0, 4.4
9''b		4.36, dd, 12.0, 2.8		4.02, dd, 11.6, 5.2
3'-OCH <sub>3</sub>	57.2	3.81, s	57.7	3.83, s
5'-OCH <sub>3</sub>	57.2	3.81, s	57.7	3.83, s
3''-OCH <sub>3</sub>	56.6	3.73, s	57.1	3.67, s
1'''	105.7	5.54, d, 8.0	105.6	5.35, d, 8.0
2'''	75.5		77.1	
3'''	79.7		80.1	
4'''	71.9	4.28–4.12, m	72.8	4.31–3.09, m
5'''	79.6		79.7	
6'''a	63.0	4.41, m	63.8	4.45, m
6'''b		4.20, m		4.30, m

#### 4. Conclusions

Five compounds were isolated from the aerial parts of *Zizania latifolia* using a prep-LC instrument equipped with cartridges of various sizes and were identified based on spectroscopic data analysis, including NMR, UV, and ESI-MS. Four flavonolignan glycosides, including two new flavonolignan glycosides, showed structural similarities in being derived from triclin-7-*O*- $\beta$ -D-glucopyranose (**1**), and were shown to be diastereomers of each other. Triclin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7-*O*- $\beta$ -D-glucopyranose (**2**) and triclin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7-*O*- $\beta$ -D-glucopyranose (**3**) were shown to be diastereomers distinguished by *threo* and *erythro* configurations, whereas triclin-4'-*O*-(*threo*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose (**4**) and triclin-4'-*O*-(*erythro*- $\beta$ -guaiacylglyceryl) ether 7''-*O*- $\beta$ -D-glucopyranose (**5**) were shown to be *threo* and *erythro*, respectively.

#### Supplementary Materials

<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and HR-ESIMS spectra of **4–5** are available as supporting data. Supplementary materials can be accessed at: <http://www.mdpi.com/1420-3049/20/04/5616/s1>.

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## Author Contributions

M.-H.B., N.-I.B., and D.-K.C. designed research; S.-S.L., Y.-S.B., and M.-C.S. performed research and analyzed the data; S.-S.L. wrote the paper. All authors read and approved the final manuscript.

## Conflicts of Interest

The authors declare no conflict of interest.

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*Sample Availability:* Samples of the compounds **1–5** are available from the authors.

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