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CHEMICAL CONSTITUENTS FROM THE AERIAL PARTS OF *Vetiveria zizanioides*

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Vetiveria zizanioides, commonly known as vetiver grass, is a perennial grass of the Poaceae family, native to India. It is traditionally used to relieve cholera, headache, rheumatism, sprains, and repel insect [1]. Previous study on vetiver grass led to the isolation of flavone derivatives [2]. There are also numerous studies on the composition of the root oil [3–6]. In the course of our search for bioactive natural products from medicinal plants, we investigated the plant.

The aerial parts of vetiver grass were collected in Zhejiang Province, People′s Republic of China in August 2009. The air-dried powdered plant material (4.5 kg) was extracted with 95% EtOH at room temperature. After evaporation of the EtOH, the viscous residue (530 g) was extracted with EtOAc. The EtOAc extract (30 g) was fractionated by column chromatography through silica gel gradient-eluting with CH_2Cl_2–MeOH (98:2–95:5–90:10–80:20–50:50) to yield A–F fractions. Fraction B (5 g) was chromatographed on Si gel eluting with CH_2Cl_2–MeOH (98:2) to obtain compound **1** (69 mg). Fraction D (6 g) was chromatographed on RP-18 gel using MeOH–H_2O (50:50–60:40–70:30) to yield 1–7 fractions: fraction 1 was subjected to Si gel column chromatography using CH_2Cl_2–MeOH (20:1) to give compound **2** (10 mg); fraction 3 eluted with CH_2Cl_2–MeOH (20:1) yielded compound **3** (12 mg) and compound **4** (30 mg). Fraction 5 was purified by Sephadex LH-20 eluting with MeOH to obtaine compound **5** (67 mg); fraction 7 was rechromatographed on RP-18 using MeOH–H_2O (70:30) to give fractions *a–d*: fraction *a* was further chromatographed on Si gel eluted with petroleum ether–acetone (1:1) to afford compounds **6** (6 mg) and **7** (10 mg); fraction *b* was subjected to Si gel column eluted with CH_2Cl_2–MeOH (12:1) followed by chromatography over a Sephadex LH-20 column eluted with MeOH to yield compounds **8** and **9** (130 mg).

On the basis of the agreement of their ESI-MS and NMR (1D and 2D) spectral data with those already published, compounds **1**–**9** were elucidated as cholesterol (**1**) [7], 1,2-bis(4-hydroxy-3-methoxyphenyl)-propane-1,3-diol (**2**) [8], 1-*O*-feruloylglycerol (**3**) [9], 1-*O*-*p*-coumaroylglycerol (**4**) [9], *trans*-*p*-hydroxycinnamic acid (**5**) [10], vladinol E (**6**) [11], vladinol F (**7**) [12], tricin 4′-*O*-(*erythro*-*β*-guaiacylglyceryl) ether (**8**), and tricin 4′-*O*-(*threo*-*β*-guaiacylglyceryl) ether (**9**) [13].

Tricin 4′-*O*-(*erythro*-*β*-Guaiacylglyceryl) Ether (8). Yellow solid, $[\alpha]_D^{20}$–42.8° (*c* 0.5, MeOH). UV (MeOH, λ_{max}, nm): 270, 303, 335. IR (KBr, ν_{max}, cm^{-1}): 3410 (OH), 2930, 1655 (C=O), 1598 and 1483 (aromatic C=C). Negative ESI-MS *m/z* 525 $[M - H]^-$. PMR (500 MHz, CD_3OD, δ, ppm, J/Hz): 6.58 (1H, s, H-3), 6.13 (2H, d, J = 2.0, H-6), 6.37 (2H, d, J = 1.0, H-8), 7.09 (2H, s, H-2′, 6′), 7.01 (1H, d, J = 2.0, H-2″), 6.74 (1H, d, J = 8.5, H-5″), 6.83 (1H, dd, J = 8.0, 1.5, H-6″), 4.95 (1H, d, J = 5.5, H-7″), 4.43 (1H, m, H-8″), 3.67 (1H, dd, J = 12.5, 3.5, H-9″*α*), 3.94 (1H, dd, J = 12.5, 5.3, H-9″*β*), 3.83 (3H, s, 3″-OMe), 3.88 (6H, s, 3′, 5′-OMe). ^{13}C NMR (125 MHz, CD_3OD, δ, ppm): 165.2 (C-2), 106.0 (C-3), 183.3 (C-4), 163.3 (C-5), 100.4 (C-6), 166.2 (C-7), 95.4 (C-8), 159.5 (C-9), 105.2 (C-10), 127.9 (C-1′), 105.6 (C-2′, 6′), 155.0 (C-3′, 5′), 140.8 (C-4′), 134.0 (C-1″), 111.9 (C-2″), 148.9 (C-3″), 147.2 (C-4″), 115.9 (C-5″), 121.0 (C-6″), 74.5 (C-7″), 87.7 (C-8″), 62.1 (C-9″), 56.6 (3″-OMe), 57.1 (3′, 5′-OMe).

Tricin 4′-*O*-(*threo*-*β*-Guaiacylglyceryl) Ether (9). Yellow solid, $[\alpha]_D^{20}$ +76.1° (*c* 0.5, MeOH). UV (MeOH, λ_{max}, nm): 270, 302, 335. IR (KBr, ν_{max}, cm^{-1}): 3409 (OH), 2930, 1655 (C=O), 1600 and 1483 (aromatic C=C). Negative ESI-MS *m/z* 525 $[M - H]^-$. PMR (500 MHz, CD_3OD, δ, ppm, J/Hz): 6.58 (1H, s, H-3), 6.13 (2H, d, J = 2.0, H-6), 6.37 (2H, d, J = 1.0, H-8), 7.09 (2H, s, H-2′, 6′), 7.04 (1H, d, J = 2.0, H-2″), 6.76 (1H, d, J = 8.5, H-5″), 6.89 (1H, dd, J = 8.0, 1.5, H-6″), 5.02 (1H, d, J = 6.5, H-7″), 4.26 (1H, m, H-8″), 3.39 (1H, dd, J = 12.0, 3.5, H-9″*α*), 3.81 (1H, dd, J = 12.0, 4.0, H-9″*β*), 3.84 (3H, s,

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3″-OMe), 3.89 (6H, s, 3′, 5′-OMe). ^{13}C NMR (125 MHz, CD_3OD, δ, ppm): 165.2 (C-2), 106.0 (C-3), 183.3 (C-4), 163.3 (C-5), 100.4 (C-6), 166.2 (C-7), 95.4 (C-8), 159.5 (C-9), 105.2 (C-10), 128.0 (C-1′), 105.6 (C-2′, 6′), 154.8 (C-3′, 5′), 141.1 (C-4′), 133.7 (C-1″), 112.1 (C-2″), 148.9 (C-3″), 147.4 (C-4″), 116.0 (C-5″), 121.1 (C-6″), 74.7 (C-7″), 89.1 (C-8″), 62.3 (C-9″), 56.6 (3″-OMe), 57.1 (3′, 5′-OMe).

To our knowledge, all compounds were isolated from *V. zizanioides* for the first time. Among them, phenylpropanoid glycerol compounds **3** and **4** were the first to be isolated from Poaceae, previously obtained from *Lilium auratum* (Liliaceae) [9]. Compounds **8** and **9**, which were reported firstly from *Vetiveria*, were rare flavonolignans with the B ring of flavone attached to the C6-C3 pigment by an ether bond at C8. This type of flavonolignan has been reported from Poaceae: *Sasa* [14], *Avena* [15], *Hyparrhenia* [13], and *Sorghum* [16] previously. The occurrence of phenylpropanoid glycerols and flavonolignans could be significant from a chemotaxonomic point of view and also add to the types of secondary metabolites of the genus *Vetiveria*.

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