

PHENOL GLYCOSIDES AND FLAVONOL GLYCOSIDES FROM THE AERIAL PART OF *Zingiber officinale*

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Ginger, the rhizomes of *Zingiber officinale* Roscoe (Zingiberaceae), has been widely used as traditional Chinese medicinal herb for centuries, and *Z. officinale* is currently widely cultivated in China. Phytochemical studies of ginger have led to the isolation and identification of numerous biologically active compounds such as gingerol, gingerone, shogaol, and diarylheptanoid, monoterpenoid, and volatile oils [1, 2]. In this paper, five phenol glycosides and five flavonol glycosides were isolated and identified from the aerial part of *Z. officinale*.

The plant of *Zingiber officinale* was collected in Tongling, Anhui Province. Its aerial part (4 kg) was extracted three times with 60% aqueous acetone at room temperature (3×18 L). The solvent was evaporated under reduced pressure to about 1 L and filtered with diatomite. Then the filtrate was subjected repeatedly to MCI gel CHP 20P, Toyopearl HW-40F, and Cosmosil 75 C18-OPN column chromatography. Finally, the ten compounds were isolated from the aerial part of *Z. officinale*. Their structures were elucidated using spectroscopic methods, the sugar part of the compounds by acid hydrolysis and comparison with authentic samples and literature. The ten compounds were identified as phenol glycosides and flavonol glycosides. Among them, four phenol glycosides (**2–5**) and four flavonol glycosides (**6–9**) were the first to be isolated from the Zingiberaceae family.

Phloroglucinol 1-O- β -D-Glucopyranoside (1). White amorphous powder, $C_{12}H_{16}O_8$ [3].

2,4-Dihydroxy-6-methoxyphenyl 1-O- β -D-Glucopyranoside (2). White amorphous powder, $C_{13}H_{18}O_9$. 1H NMR (400 MHz, D_2O , δ , ppm, J/Hz): 6.06 (1H, d, $J = 2.5$, H-3), 6.01 (1H, d, $J = 2.5$, H-5), 4.68 (1H, d, $J = 7.2$, H-1'), 3.81 (1H, dd, $J = 12.4$, 2.2, H-6'a), 3.76 (3H, s, OMe), 3.70 (1H, dd, $J = 12.5$, 5.1, H-6'b), 3.51–3.40 (3H, m, H-3', 4', 5'), 3.33 (1H, m, H-2'). ESI-MS m/z : 341.0 [$M + Na$]⁺ ($C_{13}H_{18}O_9Na$), 357.0 [$M + K$]⁺ ($C_{13}H_{18}O_9K$) [4].

3-Methoxy-4-hydroxyphenol 1-O- β -D-Glucopyranoside (3). Colorless needles, $C_{13}H_{18}O_8$. 1H NMR (400 MHz, D_2O , δ , ppm, J/Hz): 6.83 (1H, $J = 8.7$, H-5), 6.79 (1H, $J = 2.8$, H-2), 6.60 (1H, dd, $J = 8.7$, 2.8, H-6), 4.95 (1H, d, $J = 7.6$, H-1'), 3.88 (1H, dd, $J = 12.5$, 2.1, H-6'a), 3.80 (3H, s, OMe), 3.69 (1H, dd, $J = 12.5$, 6.0, H-6'b), 3.57–3.39 (4H, m, H-2', 3', 4', 5'). ESI-MS m/z : 325.0 [$M + Na$]⁺ ($C_{13}H_{18}O_8Na$), 341.0 [$M + K$]⁺ ($C_{13}H_{18}O_8K$) [5, 6].

4-Hydroxy-2-methoxyphenyl 1-O- β -D-Glucopyranoside (4). Colorless needles, $C_{13}H_{18}O_8$. 1H NMR (400 MHz, D_2O , δ , ppm, J/Hz): 7.02 (1H, d, $J = 8.8$, H-6), 6.58 (1H, d, $J = 2.8$, H-3), 6.40 (1H, dd, $J = 8.7$, 2.8, H-5), 4.92 (1H, d, $J = 8.0$, H-1'), 3.85 (1H, dd, $J = 12.3$, 1.7, H-6'a), 3.80 (3H, s, OMe), 3.70 (1H, dd, $J = 12.3$, 4.7, H-6'b), 3.54–3.42 (4H, m, H-2', 3', 4', 5'). ESI-MS m/z : 325.0 [$M + Na$]⁺ ($C_{13}H_{18}O_8Na$), 341.0 [$M + K$]⁺ ($C_{13}H_{18}O_8K$) [7].

4-Hydroxy-3,5-dimethoxyphenyl 1-O- β -D-Glucopyranoside (5). White amorphous powder, $C_{14}H_{20}O_9$. 1H NMR (400 MHz, D_2O , δ , ppm, J/Hz): 6.21 (2H, d, $J = 1.0$, H-2, 6), 4.85 (1H, d, $J = 8.0$, H-1'), 3.79 (1H, d, $J = 12.2$, H-6'a), 3.77 (6H, s, OMe), 3.66 (1H, dd, $J = 12.4$, 5.4, H-6'b), 3.50–3.39 (3H, m, H-3', 4', 5'), 3.27 (1H, ddd, $J = 9.4$, 5.5, 2.1, H-2'). ESI-MS m/z : 355.0 [$M + Na$]⁺ ($C_{14}H_{20}O_9Na$), 371.0 [$M + K$]⁺ ($C_{14}H_{20}O_9K$) [8].

Kaempferol 3-O-Rhamnosyl(1→6)glucopyranoside (6). Yellow amorphous powder, $C_{27}H_{30}O_{15}$. 1H NMR (400 MHz, CD_3OD , δ , ppm, J/Hz): 8.03 (2H, d, $J = 8.7$, H-2', 6'), 6.86 (2H, d, $J = 8.3$, H-3', 5'), 6.34 (1H, d, $J = 2$, H-8), 6.16 (1H, d, $J = 2$, H-6), 5.08 (1H, d, $J = 6.7$, H-1''), 4.48 (1H, s, H-1'''), 3.76 (1H, br.d, $J = 12.1$, H-6''a), 3.59 (1H, dd, $J = 12.1$, 5.4, H-6''b),

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3.53–3.30 (8H, m, H-2'', 3'', 4'', 5'', 2''', 3''', 4''', 5'''), 1.09 (3H, d, J = 6.1, H-6'''). ESI-MS m/z : 617.0 [M + Na]⁺ ($C_{27}H_{30}O_{15}Na$), 633.0 [M + K]⁺ ($C_{27}H_{30}O_{15}K$) [9].

Quercetin 7-O- α -L-Rhamnopyranosyl-(1→6)- β -D-glucopyranoside (7). Yellow amorphous powder, $C_{27}H_{30}O_{16}$. 1H NMR (400 MHz, CD₃OD, δ , ppm, J/Hz): 7.85 (1H, d, J = 2.1, H-6'), 7.57 (1H, dd, J = 8.4, 2.2, H-2), 6.84 (1H, d, J = 8.5, H-5'), 6.38 (1H, d, J = 2.2, H-8), 6.18 (1H, d, J = 2.0, H-6), 5.05 (1H, d, J = 7.8, H-1''), 4.49 (1H, d, J = 3.6, H-1'''), 3.81 (1H, br.d, J = 12.1, H-6''a), 3.72 (1H, dd, J = 10.0, 5.7, H-2'''), 3.62 (1H, dd, J = 12.1, 5.6, H-6''b), 3.56–3.35 (6H, m, H-2'', 3'', 4'', 5'', 3''', 5'''), 3.25 (1H, d, J = 9.4, H-4'''), 1.16 (3H, d, J = 6.2, H-6'''). ESI-MS m/z : 633.0 [M + Na]⁺ ($C_{27}H_{30}O_{16}Na$), 649.0 [M + K]⁺ ($C_{27}H_{30}O_{16}K$) [10].

Kaempferol 3-O- β -D-Glucopyranoside-7-O- α -L-rhamnopyranoside (8). Yellow amorphous powder. $C_{27}H_{30}O_{15}$. 1H NMR (400 MHz, CD₃OD, δ , ppm, J/Hz): 7.80 (2H, d, J = 8.2, H-2', 6'), 6.86 (2H, d, J = 8.4, H-3', 5'), 6.69 (1H, s, H-8), 6.58 (1H, s, H-6), 5.26 (1H, s, H-1''), 5.15 (1H, d, J = 7.4, H-1''), 3.97–3.86 (3H, m, H-6'', 2''), 3.73–3.33 (7H, m, H-2'', 3'', 4'', 5'', 3''', 4'', 5'''), 1.30 (3H, d, J = 6.1, H-6'''). ESI-MS m/z : 617.0 [M + Na]⁺ ($C_{27}H_{30}O_{15}Na$), 633.0 [M + K]⁺ ($C_{27}H_{30}O_{15}K$) [11].

Kaempferol 3-Robinoside-7-rhamnoside (9). Yellow amorphous powder. $C_{33}H_{40}O_{19}$. 1H NMR (400 MHz, D₂O, δ , ppm, J/Hz): 7.62 (2H, d, J = 8.0, H-2', 6'), 6.72 (2H, d, J = 8.1, H-3', 5'), 5.95 (1H, s, H-8), 5.74 (1H, s, H-6), 5.15 (1H, s, H-1'''), 5.09 (1H, d, J = 7.8, H-1''), 4.43 (1H, s, H-1''), 4.30 (1H, s, H-2'''), 4.10 (1H, s, H-2''), 3.96–3.86 (1H, m, H-6''a), 3.73 (5H, m, H-3'', 5'', 6''b, 5''', 5'''), 3.48 (4H, m, H-4'', 3'', 3''', 4'''), 3.25 (2H, t, J = 9.5, H-2'', 4''), 1.31 (3H, d, J = 6.0, H-6'''), 1.07 (3H, d, J = 6.0, H-6'''). ESI-MS m/z : 763.2 [M + Na]⁺ ($C_{33}H_{40}O_{19}Na$), 779.2 [M + K]⁺ ($C_{33}H_{40}O_{19}K$) [12].

Quercetin 3-O- α -L-Rhamnopyranosyl-(1→6)- β -D-glucopyranoside (10). Yellow amorphous powder, $C_{27}H_{30}O_{16}$ [13].

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