



SUPPLEMENTARY MATERIAL TO
**Improved synthesis of gastrodin, a bioactive component of a
traditional Chinese medicine**

YU-WEN LI^{1*} and CUI-LI MA²

¹School of Chemistry and Pharmacy, Qingdao Agricultural University, Qingdao 266109,
China and ²Affiliated Hospital, Qingdao Agricultural University, Qingdao 266109, China

J. Serb. Chem. Soc. 79 (10) (2014) 1205–1212

PHYSICAL, ANALYTIC AND SPECTRAL DATA

4-Methylphenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (7). Yield: 76.3 %; white crystals; m.p.: 117.0–117.8 °C; Anal. Calcd. for C₂₁H₂₆O₁₀: C, 57.53; H, 5.98 %. Found: C, 57.32; H, 6.09 %; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 2.06, 2.09, 2.12, 2.18, 2.30 (5×3H, 5×s, 4×OCOCH₃, CH₃-Ar), 3.82–3.86 (1H, m, H-4), 4.16 (1H, dd, J = 12.4 Hz, 2.4 Hz, H-6b), 4.29 (1H, dd, J = 12.4 Hz, 5.2 Hz, H-6a), 5.03 (1H, d, J = 7.2 Hz, H-1), 5.17 (1H, t, J = 9.5 Hz, H-3), 5.24–5.32 (2H, m, H-2, H-5), 6.89 (2H, d, J = 8.4 Hz, Ar-H), 7.09 (2H, d, J = 8.4 Hz, Ar-H); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 20.6, 20.7, 20.8 (4COCH₃, Ar-CH₃), 61.9 (C-6), 68.3 (C-3), 71.2 (C-5), 71.9 (C-4), 72.7 (C-2), 99.5 (C-1), 116.9, 130.0, 138.9, 154.8 (Ph), 169.3, 169.4, 170.3, 170.7 (4 COCH₃); HRMS (ESI) m/z Calcd. for C₂₁H₂₆O₁₀Na [M+Na]⁺: 461.1424. Found 461.1418; Specific rotation ([α]_D²³ / ° (c / g mL⁻¹: 1.05, CHCl₃)): –14.6.

4-(Bromomethyl)phenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (8). Yield: 91 %; white needle-like crystals; m.p.: 153–154 °C; Anal. Calcd for C₂₁H₂₅O₁₀Br: C, 48.76; H, 4.87; Br, 15.45 %. Found: C, 48.56, H, 4.61, Br, 15.29 %; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 2.05, 2.06, 2.08, 2.09 (4×3H, 4×s, 4×OCOCH₃), 3.85–3.89 (1H, m, H-4), 4.17 (1H, dd, J = 12.4 Hz, 2.4 Hz, H-6b), 4.29 (1H, dd, J = 12 Hz, 5.2 Hz, H-6a), 4.49 (2H, s, ArCH₂Br), 5.09 (1H, d, J = 7.2 Hz, H-1), 5.17 (1H, t, J = 9.2 Hz, H-3), 5.25–5.33 (2H, m, H-2, H-5), 6.96 (2H, dd, J = 6.8 Hz, 3.0 Hz, Ar-H), 7.33 (2H, dd, J = 6.8 Hz, 3.0 Hz, Ar-H); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 20.7, 20.8 (4×COCH₃), 33.2 (ArCH₂Br), 61.9 (C-6), 68.2 (C-3), 71.1 (C-5), 72.1 (C-4), 72.6 (C-2), 98.8 (C-1), 117.1, 130.5, 132.8, 156.7 (C-Ar), 169.3, 169.4, 170.3, 170.6 (4 × COCH₃); HRMS

*Corresponding author. E-mail: ywli@qau.edu.cn

(ESI) m/z Calcd. for $C_{21}H_{25}O_{10}^{81}BrNa$ $[M+Na]^+$: 541.0508. Found: 541.0514; Specific rotation ($[\alpha]_D^{23} / ^\circ (c / g\ mL^{-1}: 1.00, CHCl_3)$): -13.4.

4-(Hydroxymethyl)phenyl 2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside (5). Yield: 93 %; white crystals; m.p.: 108.9–109.7 °C; Anal. Calcd. for $C_{21}H_{26}O_{11}$: C, 55.50; H, 5.77 %. Found: C, 55.27, H, 5.49 %; 1H -NMR (400 MHz, $CDCl_3$, δ / ppm): 2.04, 2.05, 2.06, 2.08 (4 $\times$ 3H, 4 $\times$ s, 4 $\times$ OCOCH₃), 3.84–3.88 (1H, *m*, H-5), 4.18 (1H, *dd*, $J = 12.4$ Hz, 4.2 Hz, H-6a), 4.29 (1H, *dd*, $J = 12.4$ Hz, 5.2 Hz, H-6b), 4.64 (2H, *s*, ArCH₂OH), 5.07 (1H, *d*, $J = 7.2$ Hz, H-1), 5.16 (1H, *t*, $J = 9.6$ Hz, H-4), 5.24–5.32 (2H, *m*, H-2, H-5), 6.98 (2H, *d*, $J = 8.4$ Hz, Ar-H), 7.27–7.31 (2H, *m*, Ar-H); ^{13}C -NMR (100 MHz, $CDCl_3$, δ / ppm): 20.6, 20.7 (4 COCH₃), 61.9 (C-6), 64.7 (ArCH₂OH), 68.3 (C-4), 71.2 (C-2), 72.0 (C-3), 72.7 (C-5), 99.2 (C-1), 117.1, 128.5, 136.0, 156.4 (C-Ar), 169.3, 169.4, 170.3, 170.6 (4 COCH₃); HRMS (ESI) m/z Calcd. for $C_{21}H_{26}O_{11}Na$ $[M+Na]^+$: 447.1373. Found: 447.1378; Specific rotation ($[\alpha]_D^{23} / ^\circ (c / g\ mL^{-1}: 1.00, CHCl_3)$): -12.4.

4-(Hydroxymethyl)phenyl β -D-glucopyranoside (1). Yield: 90 %; white crystals; m.p.: 154–155 °C (lit.¹ 153–155 °C); Anal. Calcd for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34 %. Found: C, 54.37, H, 6.42 %; 1H -NMR (400 MHz, CD_3OD , δ / ppm): 3.32–3.49 (4H, *m*, H-2, H-3, H-4, H-5), 3.72 (1H, *dd*, $J = 12.4$ Hz, 5.2 Hz, H-6a), 3.91 (1H, *dd*, $J = 12.0$ Hz, 1.6 Hz, H-6b), 4.56 (2H, *s*, ArCH₂OH), 4.91 (1H, *d*, $J = 7.6$ Hz, H-1), 7.09 (2H, *d*, $J = 8.8$ Hz, Ar-H), 7.29 (2H, *d*, $J = 8.8$ Hz, Ar-H); ^{13}C -NMR (100 MHz, CD_3OD , δ / ppm): 61.1 (C-6), 63.4 (ArCH₂OH), 69.9 (C-4), 73.5 (C-2), 76.6 (C-5), 76.7 (C-3), 100.9 (C-1), 116.2, 128.0, 135.2, 157.1 (C-Ar); HRMS (ESI) m/z Calcd. for $C_{13}H_{18}O_7Na$ $[M+Na]^+$: 309.0949. Found: 309.0945; Specific rotation ($[\alpha]_D^{23} / ^\circ (c / g\ mL^{-1}: 0.85, MeOH)$): -52.2.

REFERENCE

1. L. L. Fan, Y. C. Dong, T. Y. Xu, H. F. Zhang, Q. H. Chen, *Appl. Biochem. Biotechnol.* **170** (2013) 138.