A new epicatechin glucopyranoside derivative from *Styrax suberifolius*

Bing-lei Liu\(^a,c\), Xin Hu\(^a\), Hua-liang He\(^a\), Lin Qiu\(^a\), You-zhi Li\(^a,b\) and Wen-bing Ding\(^a,b\)

\(^a\)Hunan Provincial Engineering & Technology Research Center for Biopesticide and Formulation Processing, Hunan Agricultural University, Changsha, China; \(^b\)National Research Center of Engineering & Technology for Utilization of Botanical Functional Ingredients, Hunan Agricultural University, Changsha 410128, China; \(^c\)Hunnan Cotton Science Institute, Changde 415100, China

A new derivative of epicatechin glucopyranoside, \((2R,3R)-3,7,4\'-\text{trihydroxy-5,3'}-\text{dimethoxyflavan} ~ 7-O-\beta-D\text{-glucopyranoside (1)},\) together with three mononuclear phenolic acid esters, methyl orsellinate (2), ethyl orsellinate (3) and methyl \(\beta\)-orcinolcarboxylate (4) were isolated from the bark of *Styrax suberifolius*. The structures of 1–4 were determined on the basis of extensive analysis of NMR and MS spectra combined with chemical hydrolysis. The antifungal activities of the isolated compounds against three plant pathogenic fungi, *Alternaria solani, Fusarium oxysporum* and *Phomopsis cytospore* were evaluated using radial growth inhibition assay. Compounds 2, 3 and 4 exerted selective inhibitory activities against the tested fungi. Among of them, methyl \(\beta\)-orcinolcarboxylate (4) exhibited obvious inhibitory effect against *P. cytospore*, with an inhibition rate of 86.72% at 100 \(\mu\)g/ml.

Keywords: *Styrax suberifolius*; epicatechin derivative; flavonoid glycoside; antifungal activity.

1. The HR-ESIMS, CD and NMR spectra of compound 1

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Figure S1. HR-ESIMS of compound 1

Figure S2. CD spectrum of compound 1
Figure S3. $^1$H-NMR of compound 1

Figure S4. $^{13}$C-NMR of compound 1
Figure S5. $^1$H-$^1$H COSY of compound 1

Figure S6. HSQC of compound 1
Figure S7. HMBC of compound 1

Figure S8. NOESY of compound 1
2. The NMR and ESIMS data of known compounds 2–4

2.1. Methyl orsellinate (2)
Colorless needles (MeOH); $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$: 11.76 (1H, s, OH-2), 6.28 (1H, d, $J = 2.5$ Hz, H-5), 6.23 (1H, d, $J = 2.5$ Hz, H-5), 3.92 (3H, s, -OCH$_3$), 2.49 (3H, s, CH$_3$-2); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$: 172.0 (-COO-), 165.3 (C-2), 160.2 (C-4), 143.9 (C-6), 111.3 (C-5), 105.8 (C-1), 101.3 (C-3), 51.7 (-OCH$_3$), 24.1 (CH$_3$-2). Positive ion ESI-MS $m/z$ 183 [M + H]$^+$, 205 [M + Na]$^+$, and negative ESIMS $m/z$: 181 [M − H]$^−$.

2.2. Ethyl orsellinate (3)
Colorless needles (MeOH); $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$: 11.85 (1H, s, OH-2), 6.28 (1H, d, $J = 2.5$ Hz, H-5), 6.23 (1H, d, $J = 2.5$ Hz, H-5), 4.39 (2H, q, $J = 7.1$ Hz, -OCH$_2$-), 1.41 (3H, t, $J = 7.1$ Hz, -OCH$_2$-CH$_3$); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$: 171.8 (-COO-), 165.5 (C-2), 160.3 (C-4), 144.2 (C-6), 111.5 (C-5), 106.0 (C-1), 101.4 (C-3), 61.5 (-OCH$_2$-), 24.5 (CH$_3$-6), 14.4 (-OCH$_2$-CH$_3$). Positive ion ESI-MS $m/z$ 197 [M + H]$^+$, and negative ESIMS $m/z$: 195 [M − H]$^−$, 391 [2M − H]$^−$.

2.3. Methyl $\beta$-Orcinolcarboxylate (4)
Colorless needles (MeOH); $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$: 12.04 (1H, s, OH-2), 6.20 (1H, s, H-5), 5.29 (1H, brs, OH-4), 3.92 (3H, s, -OCH$_3$), 2.45 (3H, s, CH$_3$-6), 2.10 (3H, s, CH$_3$-3); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$: 172.6 (-COO-), 163.1 (C-2), 158.1 (C-4), 140.2 (C-6), 110.6 (C-1), 108.5 (C-5), 105.2 (C-3), 51.8 (-OCH$_3$), 24.1 (CH$_3$-6), 7.7 (CH$_3$-3). Positive ion ESI-MS $m/z$ 197 [M + H]$^+$, 393 [2M + H]$^+$, and negative ESIMS $m/z$: 195 [M − H]$^−$. 