SUPPLEMENTARY MATERIAL

Two novel prenylated kaempferol derivatives from fresh bud’s fur of *Platanus acerifolia* and their anti-proliferative activities

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Two novel prenylated kaempferol derivatives (1, 2), together with seven known metabolites were isolated from ethanol extract of fresh *Platanus acerifolia* bud’s fur by multistep chromatographic processing. Structure of compounds 1 and 2 was confirmed by 1D, 2D NMR spectra and HR-ESI-MS. In addition, compound 1 was further analyzed by X-ray crystallography. Anti-proliferative activities *in vitro* against human breast carcinoma (MCF-7) and human hepatocellular carcinoma (Hep-G2) cell lines for compound 1, 2, and 8 were evaluated. Compound 1 exhibited cytotoxic activity toward MCF-7 and Hep-G2 cell lines with the IC50 values 38.2 and 39.5 μM, respectively. Moreover, compound 2 showed weak cytotoxic activities against the two cell lines.

**Keywords:** *Platanus acerifolia*; Platanaceae; C-prenyl kaempferol; cytotoxic

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Fig. S1 $^1$H NMR Spectrum of compound 1

Fig. S2 $^{13}$C NMR Spectrum of compound 1

Fig. S3 HMBC spectrum of compound 1

Fig. S4 COSY spectrum of compound 1

Fig. S5 HSQC spectrum of compound 1

Fig. S6 HR-ESI-MS of compound 1

Fig. S7 $^1$H NMR Spectrum of compound 2

Fig. S8 $^{13}$C NMR Spectrum of compound 2

Fig. S9 HMBC spectrum of compound 2

Fig. S10 COSY spectrum of compound 2

Fig. S11 HSQC spectrum of compound 2

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Fig. S13 Chemical structure of compound 1 to 9

Fig. S14 Key HMBC and $^1$H-$^1$H COSY correlations of the new compounds 1, 2.

Fig. S15 IR spectra of compounds 1.

Fig. S16 IR spectra of compounds 2.

Table S1 $^1$H, $^{13}$C NMR data of 1 in CDC$_3$ and 2 in DMSO-$d_6$ ($\delta$ in ppm; $J$ in Hz)
**X-ray Crystallography**

Single-crystal X-ray diffraction data of compound 1 were collected using a Rigaku Saturn 924 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Data processing including empirical absorption correction was performed using the CrystalClear software package (Rigaku, 2005). The crystal structure was solved by direct methods and then refined by full-matrix least-squares refinements on $F^2$ using the SHELXLTL software package (SHELX-97). All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. All hydrogen atoms were placed at ideal positions and refined using “riding” model. Crystal data, data collection and structure refinement details are summarized in Table 1.

**Table 1. Crystal Data and Structure Refinement for Compound 1 at 293 K.**

| Moiety formula | $C_{21}H_{20}O_7$ |
|---------------|------------------|
| Formula weight | 384.4            |
| Crystal system | triclinic        |
| Space group   | P-1              |
| $a$ (Å)       | 9.454(19)        |
| $b$ (Å)       | 10.336(2)        |
| $c$ (Å)       | 12.045(2)        |
| $\alpha$ (°) | 73.64(3)         |
| $\beta$ (°)  | 82.17(3)         |
| $\gamma$ (°) | 63.21(3)         |
| Volume (Å³), Z| 1008.1(4), 2     |
| Absorption coefficient | 0.105       |
| $F(000)$      | 440              |
| Collected, independent and observed reflections | 3654           |
| $[I>2\sigma(I)]$ | 1542          |
| $R[F^2>2(F^2)]$, $wR(F^2)$ | 0.1218, 0.2781 |
| $S$           | 1.075            |

The title compound was dissolved in the methanol solution, suitable pale-yellow block-shaped single crystals were obtained by slow evaporation of the methanol solution at room temperature. Single-crystal X-ray diffraction reveals that compound 1 crystallizes in the triclinic space group P-1 and it is characterized with the formula $C_{21}H_{20}O_7\cdot CH_3OH$, including the methanol molecule. It should be noted that all the C–O bond lengths maintain the equivalence, with lengths in the 1.347(6)–1.384(5) Å range, except for C4–O2 with 1.295(5) Å, indicates the existence of carbonyl group.
Fig. S1 ¹H NMR Spectrum of compound 1

Fig. S2 ¹³C NMR Spectrum of compound 1
Fig. S3 HMBC spectrum of compound 1

Fig. S4 COSY spectrum of compound 1
Fig. S5 HSQC spectrum of compound 1

Fig. S6 HR-ESI-MS of compound 1
Fig. S7 $^1$H NMR Spectrum of compound 2

Fig. S8 $^{13}$C NMR Spectrum of compound 2
Fig. S9 HMBC spectrum of compound 2

Fig. S10 COSY spectrum of compound 2
Fig. S11 HSQC spectrum of compound 2

Fig. S12 HR-ESI-MS of compound 2
Fig. S13 Chemical structure of compound 1 to 9

Fig. S14 Key HMBC and $^1$H-$^1$H COSY correlations of the new compounds 1, 2.
Fig. S15 IR spectra of compounds 1.

Fig. S16 IR spectra of compounds 2.
Table S1

$^1$H, $^{13}$C NMR data of 1 in CDCl$_3$ and 2 in DMSO-$d_6$ ($\delta$ in ppm; $J$ in Hz)

| Position | $^1$H NMR  | $^{13}$C NMR  | $^1$H NMR  | $^{13}$C NMR  |
|----------|------------|--------------|------------|--------------|
| 2        | 146.4      |              | 150.3      |              |
| 3        | 135.4      |              | 137.0      |              |
| 4        | 175.5      |              | 176.8      |              |
| 5        | 159.5      |              | 161.4      |              |
| 6        | 6.32 (1H, s) | 100.9       | 6.20 (1H, d, 2.0) | 98.7       |
| 7        | 161.7      |              | 164.3      |              |
| 8        | 109.9      |              | 93.9       |              |
| 9        | 155.4      |              | 157.2      |              |
| 10       | 104.8      |              | 104.0      |              |
| 1'       | 122.8      |              | 120.8      |              |
| 2'       | 7.67 (1H, s) | 110.6       | 6.72 (1H, s) | 116.8      |
| 3'       | 146.3      |              | 145.9      |              |
| 4'       | 147.6      |              | 148.7      |              |
| 5'       | 7.09 (1H, d, 8.4) | 114.7 | 7.00 (1H, s) | 114.5      |
| 6'       | 7.70 (1H, dd, 8.4, 1.8) | 122.4 |              | 134.5      |
| 1''      | 40.6       |              | 3.17 (2H, d, 5.4) | 31.7       |
| 2''      | 6.50 (1H, dd, 10.4, 18.0) | 148.8 | 5.11 (1H, t, 7.2) | 123.7      |
| 3''      | 5.42 (1H, brd, 10.0) | 114.0 |              | 131.7      |
|          | 5.49 (1H, brd, 18.0) |         |              |              |
| 1''-CH$_3$ | 1.72 (6H, s) | 27.8 |              |              |
| 3''-OCH$_3$ | 3.97 (3H, s) | 56.0 | 3.75 (3H, s) | 56.4       |
| 4''-OH | 5.99 (1H, s) |              | 9.43 (1H, s) |              |
| 3-OH | 6.61 (1H, s) |              | 8.98 (1H, s) |              |
| 5-OH | 12.18 (1H, s) |              | 12.53 (1H, s) |              |
| 7-OH | 7.34 (1H, s) |              | 10.77 (1H, s) |              |

$^a$ $^1$H and $^{13}$C NMR spectra were obtained at 400 and 100 MHz.

$^b$ $^1$H and $^{13}$C NMR data of 3''-CH$_3$ were $\delta_c$ 25.9 and 18.0, corresponding to $\delta$ 1.57 (3H, s), $\delta$ 1.47 (3H, s).