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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Legends for Figures and Tables

Fig. S1 ^1H 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 ^1H 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 ^1H - ^1H COSY correlations of the new compounds **1**, **2**.

Fig. S15 IR spectra of compounds **1**.

Fig. S16 IR spectra of compounds **2**.

Table S1 ^1H , ^{13}C NMR data of **1** in CDCl_3 and **2** in $\text{DMSO}-d_6$ (δ 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-K α radiation ($\lambda = 0.71073 \text{ \AA}$). 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	<i>P</i> -1
<i>a</i> (Å)	9.454(19)
<i>b</i> (Å)	10.336(2)
<i>c</i> (Å)	12.045(2)
α (°)	73.64(3)
β (°)	82.17(3)
γ (°)	63.21(3)
Volume (Å ³), <i>Z</i>	1008.1(4), 2
Absorption coefficient	0.105
<i>F</i> (000)	440
Collected, independent and observed reflections	3654 3654 1542
[$I > 2\sigma(I)$]	
$R[F^2 > 2(F^2)]$, $wR(F^2)$	0.1218, 0.2781
<i>S</i>	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 C₂₁H₂₀O₇·CH₃OH, 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 ^1H 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 ^1H - ^1H COSY correlations of the new compounds 1, 2.

Fig. S15 IR spectra of compounds 1.

Fig. S16 IR spectra of compounds 2.

Table S1**¹H, ¹³C NMR data of 1 in CDCl₃ and 2 in DMSO-*d*₆ (δ in ppm; *J* in Hz)**

Position	1 ^a		2 ^{ab}	
	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	6.32 (1H, d, 2.0)	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) 5.49 (1H, brd, 18.0)	114.0		131.7
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 ¹H and ¹³C NMR spectra were obtained at 400 and 100 MHz.^b ¹H and ¹³C NMR data of 3``-CH₃ were δ_c 25.9 and 18.0, corresponding to δ 1.57 (3H, s), δ 1.47 (3H, s).