SUPPLEMENTARY MATERIAL

Two new cytotoxic glycosides isolated from the green walnut husks of *Juglans mandshurica* Maxim.

Yuan-Yuan Zhou^a, Quan-Yu Liu^b, Bing-You Yang^a, Yan-Qiu Jiang^a, Yu-Xin Liu^a, Ying Wang^a, Shuang Guo^a and Haixue Kuang^{a*}

^aCollege of Pharmacy, Heilongjiang University of Chinese Medicine, Harbin 150040, P. R. China;

^bQuality Testing Branch, Veterinary Drug and Feed Supervision Institute of Heilongjiang Province, Harbin 150040, P. R. China

Abstract:

Two new glycosides including an alcohol glycoside and a phenolic glycoside, hexyl-1-*O*- α -D-arabinofuranosyl-(1 $\rightarrow$ 6)- β -D-glucopyranoside (1), 4-hydroxypropio-phenone-4-*O*- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranoside(2), along with eight known naphthalenyl glucosides (3-8) were isolated from green walnut husks of *Juglans mandshurica*, and their structures were elucidated on the basis of spectroscopic studies. All compounds were evaluated for their inhibitory effects on tumor cells (BGC-823, HepG-2, MCF-7). The results showed that new compounds 1 and 2 showed superior inhibitory activity in comparison with other naphthalenyl glucosides.

Keywords: *Juglans mandshurica*; alcohol glycoside; phenolic glycoside; cytotoxic activity

Table of Contents

S2:	Table S1: NMR spectroscopic data of compound 1
S3:	Table S2: NMR spectroscopic data of compound 2
S4:	Table S3: IC ₅₀ values of compounds 1-8 and positive control
S4:	Figure S1: Key HMBC(H→C) correlations of compounds 1 and 2
S5:	Figure S2: ¹ H-NMR spectrum of the new compound 1 in Methanol-d ₄
S5:	Figure S3: ¹³ C-NMR spectrum of the new compound 1 in Methanol-d ₄
S6:	Figure S4: DEPT spectrum of the new compound 1 in Methanol-d ₄
S6:	Figure S5: HSQC spectrum of the new compound 1 in Methanol-d ₄
S7:	Figure S6: HMBC spectrum of the new compound 1 in Methanol-d ₄
S8:	Figure S7: ¹ H-NMR spectrum of the new compound 2 in Methanol-d ₄
S8:	Figure S8: ¹³ C-NMR spectrum of the new compound 2 in Methanol-d ₄
S9:	Figure S9: DEPT spectrum of the new compound 2 in Methanol-d ₄
S9:	Figure S10: HSQC spectrum of the new compound 2 in Methanol-d ₄
S10:	Figure S11: HMBC spectrum of the new compound 2 in Methanol-d ₄

Table S1. NMR spectroscopic data of compound 1 (δ values in ppm, J values in Hz)

No.	^1H -NMR	^{13}C -NMR	DEPT	HMBC (H $\rightarrow$ C)
1	3.86 <i>dt</i> (9.6, 6.8) 3.53 <i>dt</i> (9.6, 6.8)	71.1	CH_2	C-1', C-2, C-3
2	1.61 <i>dt</i> (14.9, 6.8) 2H	30.8	CH_2	C-1, C-3, C-4
3	1.28-1.35 <i>m</i> 6H	26.8	CH_2	
4		32.9	CH_2	
5		23.7	CH_2	
6	0.90 <i>t</i> 3H (6.8)	14.4	CH_3	C-4, C-5
1'	4.24 <i>d</i> (7.8)	104.4	CH	C-1, C-2', C-3'
2'	3.15 <i>dd</i> (8.8, 7.8)	75.1	CH	C-1', C-3'
3'	3.34 <i>t</i> (8.8)	78.1	CH	C-4'
4'	3.25 <i>t</i> (9.0)	72.0	CH	C-5'
5'	3.42 <i>ddd</i> (9.0, 5.9, 2.3)	76.7	CH	C-4'
6'	4.01 <i>dd</i> (11.0, 2.3) 3.59 <i>dd</i> (11.0, 5.0)	68.1	CH_2	C-1'', C-4', C-5'
1''	4.95 <i>d</i> (1.1)	110.0	CH	C-6', C-2'', C-3''
2''	3.96 <i>m</i>	86.0	CH	C-1''
3''	3.81 <i>dd</i> (3.6, 6.2)	79.0	CH	C-4'', C-5''
4''	3.98 <i>m</i>	83.3	CH	C-3''
5''	3.73 <i>dd</i> (11.6, 3.4) 3.63 <i>dt</i> (11.6, 5.3)	63.1	CH_2	C-3''

Table S2. NMR spectroscopic data of compound 2 (δ values in ppm, J values in Hz)

No.	^1H -NMR	^{13}C -NMR	DEPT	HMBC (H $\rightarrow$ C)
1		132.4	C	
2	7.98 <i>d</i> (8.9)	131.4	CH	C-3, C-7
3	7.19 <i>d</i> (8.9)	117.4	CH	C-2, C-4
4		162.8	C	
5	7.19 <i>d</i> (8.9)	117.4	CH	C-4, C-6
6	7.98 <i>d</i> (8.9)	131.4	CH	C-5, C-7
7		202.2	C	
8	3.02 <i>q</i> (7.2)	32.4	CH ₂	C-7, C-9
9	1.17 <i>t</i> (7.2)	8.8	CH ₃	C-8
1'	5.02 <i>d</i> (7.6)	101.5	CH	C-4, C-2'
2'	3.22 <i>m</i>	75.2	CH	C-1', C-3'
3'	3.29 <i>m</i>	78.0	CH	C-4'
4'	3.39 <i>m</i>	71.4	CH	C-3'
5'	3.17 <i>m</i>	77.9	CH	
6'	4.17 <i>dd</i> (1.5, 11.6)	69.8	CH ₂	C-5', C-1''
	3.81 <i>dd</i> (5.8, 11.6)			
1''	4.37 <i>d</i> (7.7)	104.7	CH	C-2'', C-6'
2''	3.49 <i>m</i>	74.8	CH	C-1'', C-3''
3''	3.29 <i>m</i>	78.0	CH	C-4''
4''	3.29 <i>m</i>	71.6	CH	C-3''
5''	3.49 <i>m</i>	77.8	CH	
6''	3.74 <i>dd</i> (11.1, 5.3)	62.7	CH ₂	C-5''
	3.64 <i>m</i>			

Table S3

COMPOUNDS	IC ₅₀ (μM) tumor cells lines ($\bar{x} \pm SD$, n=3)		
	BGC-823	HepG-2	MCF-7
1	51.47±2.56	56.43±2.22	67.12±5.14
2	28.15±4.88	22.64±4.02	35.17±3.28
3	98.51±4.96	-*	-
4	-	92.14±1.98*	-
5	-	-*	-
6	-	87.97±3.37*	-
7	-	-*	-
8	-	-*	-
cisplatin	8.14±1.09	4.51±2.66*	6.68±2.11

* the data was obtained from previous experiment, see reference:
doi: 10.3390/molecules200915572

Figure S1: Key HMBC correlations of compounds 1 and 2

Figure S2: ^1H -NMR spectrum of the new compound 1 in Methanol- d_4

Figure S3: ^{13}C -NMR spectrum of the new compound 1 in Methanol- d_4

Figure S4: DEPT spectrum of the new compound 1 in Methanol-d₄

Figure S5: HSQC spectrum of the new compound 1 in Methanol-d₄

Figure S6: HMBC spectrum of the new compound 1 in Methanol-d₄

Figure S7: ^1H -NMR spectrum of the new compound 2 in Methanol- d_4

Figure S8: ^{13}C -NMR spectrum of the new compound 2 in Methanol- d_4

Figure S9: DEPT spectrum of the new compound 2 in Methanol-d₄

Figure S10: HSQC spectrum of the new compound 2 in Methanol-d₄

Figure S11: HMBC spectrum of the new compound 2 in Methanol-d₄