SUPPLEMENTARY MATERIAL

Two new triterpenoid glycosides from the stems of *Camellia oleifera*

Abel.

Qing-Wei Yan^{a,b}, Hui-Zheng Fu^{a*}, Yue-Hua Luo^a, Guo-Ping Zhou^a, Kai-Hua Wan^c
and Rui-Jian Zhong^{a*}

^a Jiangxi Provincial Institute for Drug Control, Jiangxi Provincial Engineering Research Center for Drug and Medical Device Quality, Nanchang 330029, Jiangxi, P. R. China

^b Pharmaceutical Department of Nanchang University, Nanchang 330006, Jiangxi, P. R. China

^c Drug Adverse Reaction Monitoring Center of Jiangxi, Nanchang 330046, Jiangxi, P. R. China

Two new oleanane-type triterpenoid glycosides, 3-*O*- β -D-xylopyranosyl-(1 $\rightarrow$ 2)- α -L-arabinopyranosyl-(1 $\rightarrow$ 3)-[β -D-glucuronopyranosyl-(1 $\rightarrow$ 2)]- β -D-glucuronopyranosyl-22 α -angeloyloxyolean-12-ene-15 α ,16 α ,28-triol(1) and 3-*O*- β -D-xylopyranosyl-(1 $\rightarrow$ 2)- α -L-arabinopyranosyl-(1 $\rightarrow$ 3)-[β -D-glucuronopyranosyl-(1 $\rightarrow$ 2)]- β -D-glucuronopyranosyl-21 β -acetyl-22 α -angeloyloxyolean-12-ene-16 α ,28-diol (2) were isolated from the stems of *Camellia oleifera* Abel. Their structures were elucidated by means of spectroscopic methods and chemical evidence. The cytotoxic activities of compounds 1-2 were evaluated against five human tumor cell lines (HCT-8, BGC-823, A549, and A2780). Compounds 1-2 showed cytotoxic activity against five human cancer cell lines, with IC₅₀ values ranging from 3.15 to 7.32 μ M.

Keywords: *Camellia oleifera* Abel.; theaceae; triterpenoid glycosides

*Corresponding author. E-mail: fhzhf620@sohu.com; zhongrj@jxfda.gov.cn

Supplemental Information

Table 1. ^1H and ^{13}C NMR spectral data of compounds **1** and **2** in $\text{C}_5\text{D}_5\text{N}$ (δ in ppm, J in Hz).

position	1 ^a		2 ^b	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}
1	1.30 (1H, m)	39.1	1.27 (1H, m)	39.2
	0.80 (1H, m)		0.74 (1H, m)	
2	2.08 (1H, m)	26.6	2.08 (1H, m)	27.0
	1.79 (1H, m)		1.78 (1H, m)	
3	3.20 (1H, dd, 12.6, 4.8 Hz)	89.7	3.24 (1H, dd, 12.0, 4.0 Hz)	89.9
4		39.6		40.0
5	0.76 (1H, brd, 12.0 Hz)	55.6	0.73 (1H, m)	56.1
6	1.52 (1H, m)	18.8	1.57 (1H, m)	18.8
	1.36 (1H, m)		1.35 (1H, m)	
7	2.07 (1H, m)	37.0	1.31 (1H, m)	35.3
	2.00 (1H, m)		1.61 (1H, m)	
8		44.4		40.5
9	1.68 (1H, m)	47.1	1.61 (1H, m)	47.5
10		36.6		36.7
11	1.85 (1H, m)	24.1	1.81 (1H, m)	24.2
	1.80 (1H, m)		1.78 (1H, m)	
12	5.49 (1H, br s)	124.9	5.40 (1H, br s)	123.5
13		144.4		143.2
14		48.1		40.5
15	4.31 (1H, m)	67.6	1.59 (1H, m)	33.5
			2.12 (1H, m)	
16	4.42 (1H, m)	78.3	4.49 (1H, m)	69.1
17		46.1		47.3
18	2.76 (1H, m)	41.5	3.04 (1H, brd, 12.0 Hz)	42.1
19	2.87 (1H, m)	47.3	3.03 (1H, m)	48.4
	1.28 (1H, m)		1.40 (1H, m)	
20		31.8		37.2
21	2.88 (1H, m)	42.5	6.58 (1H, d, 10.5 Hz)	79.8
	2.74 (1H, m)			
22	4.31 (1H, dd)	72.9	6.30 (1H, d, 10.5 Hz)	73.1
23	1.16 (3H, s)	28.0	1.21 (3H, s)	28.3
24	1.03 (3H, s)	16.8	1.07 (3H, s)	17.1
25	0.79 (3H, s)	15.8	0.79 (3H, s)	16.1
26	1.12 (3H, s)	17.8	0.83 (3H, s)	17.3
27	1.83 (3H, s)	21.3	1.84 (3H, s)	28.0
28	4.30 (1H, d, 10.2 Hz)	63.7	3.65 (1H, d, 10.0 Hz)	63.9

	4.48 (1H, d, 10.2 Hz)		3.41 (1H, d, 10.0 Hz)	
29	1.04 (3H, s)	33.7	1.07 (3H, s)	29.9
30	1.14 (3H, s)	25.3	1.31 (3H, s)	20.5
1'		167.7		168.6
2'		128.3		129.5
3'	5.90 (1H, q, 6.6 Hz)	138.3	5.91 (1H, q, 7.0 Hz)	137.5
4'	1.98 (3H, d, 6.6 Hz)	15.9	2.08 (3H, d, 7.0 Hz)	16.3
5'	1.91 (3H, s)	20.9	1.95 (3H, s)	21.5
OAc				
1				171.6
2			2.02 (3H, s)	21.3
Sugar (C-3)				
GlcA 1	4.81 (1H, d, 7.8 Hz)	105.6	4.91 (1H, d, 7.0 Hz)	106.1
2	4.63 (1H, m)	78.4	4.68 (1H, m)	79.1
3	4.42 (1H, m)	84.8	4.42 (1H, m)	84.2
4	4.48 (1H, m)	71.1	4.51 (1H, m)	71.6
5	4.47 (1H, m)	172.1	4.57 (1H, m)	172.2
6				
Ara(1→3)GlcA				
1	5.69 (1H, d, 7.8 Hz)	101.9	5.78 (1H, d, 7.0 Hz)	102.3
2	4.50 (1H, m)	83.8	4.57 (1H, m)	82.7
3	4.71 (1H, m)	73.5	4.30 (1H, m)	74.1
4	4.53 (1H, m)	68.9	4.33 (1H, m)	68.7
5	4.54 (1H, m)	66.2	3.76 (1H, d, 11.5 H)	66.3
	4.36 (1H, m)		4.42 (1H, m)	
Xyl(1→3)Ara				
1	5.01 (1H, d, 8.4 Hz)	107.7	5.00 (1H, d, 6.5 Hz)	107.5
2	4.22 (1H, m)	75.1	4.11 (1H, m)	76.1
3	4.42 (1H, m)	78.3	3.99 (1H, m)	78.7
4	4.44 (1H, m)	70.6	4.24 (1H, m)	71.1
5	3.40 (1H, t, 11.4 Hz)	67.6	3.47 (1H, t, 11.5 Hz)	68.0
	4.38 (1H, m)		4.40 (1H, m)	
Glc(1→2) GlcA				
1	5.98 (1H, d, 8.4 Hz)	102.4	5.91 (1H, d, 5.5 Hz)	103.1
2	4.29 (1H, m)	76.0	4.30 (1H, m)	76.9
3	4.30 (1H, m)	77.1	4.35 (1H, m)	77.9
4	4.45 (1H, m)	69.8	4.42 (1H, m)	73.1
5	4.07 (1H, m)	76.5	4.38 (1H, m)	78.7
6	4.34 (1H, m)	61.9	4.13 (1H, m)	63.9
			4.23 (1H, m)	

^a Measured in C₅D₅N at 600MHz for ¹H NMR, and 125 MHz for ¹³C NMR, respectively.

^b Measured in C₅D₅N at 500MHz for ¹H NMR, and 100 MHz for ¹³C NMR, respectively.

Table 2. Cytotoxicity of the extract and compounds **1-2**.

Compound	IC ₅₀ (μM)				
	HCT-8	Bel-7402	BGC-823	A-549	A2780
The extract ^a	7.10±1.02 ^{***}	9.18±1.42 ^{***}	9.23±1.34 ^{***}	9.23±1.52 ^{***}	7.88±1.42 ^{***}
1	12.02±1.89 ^{***}	5.50±0.73 ^{***}	5.81±0.45 ^{***}	6.24±1.03 ^{***}	7.27±1.23 ^{***}
2	7.32±0.93 ^{***}	3.15±0.78 ^{***}	4.68±0.75 ^{***}	5.93±0.64 ^{***}	3.36±0.47 ^{***}
Paclitaxel ^b	(5.15±0.25)×10 ⁻²	(6.06±0.89)×10 ⁻³	(3.43±0.23)×10 ⁻³	(4.40±0.41)×10 ⁻³	(8.05±1.02)×10 ⁻³

^a The *n*-BuOH part of the 95% EtOH extract of the stems of *C. oleifera*; ^b Positive control. *n*=3. ****P*<0.001 vs Paclitaxel.

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S1 UV Spectrum of Compound 1

MS Formula Results: + Scan (7.898 min) Sub (201006184.d)

m/z	Ion	Formula	Abundance
1197.5668	(M+Na) ⁺	C57 H90 Na O25	42925.4

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DRE
✓	C57 H90 O25	C57 H90 Na O25	1197.5663	99.08		1174.5776	1174.5771	-0.42	0.42	97.81	99.4	99.68	1197.5668	13
✓	C50 H94 O30	C50 H94 Na O30	1197.5722	81.24		1174.5776	1174.583	4.58	4.58	87.6	99.57	68.26	1197.5668	4

S2 HRESIMS Spectrum of Compound 1

S3 ¹H NMR Spectrum of Compound **1** in Pyridine-*d*₅

S4 ¹³C NMR Spectrum of Compound **1** in Pyridine-*d*₅

S5 HSQC Spectrum of Compound **1** in Pyridine- d_5

S6 HMBC Spectrum of Compound **1** in Pyridine- d_5

S7 ^1H - ^1H COSY Spectrum of Compound **1** in Pyridine- d_5

S8 NOESY Spectrum of Compound **1** in Pyridine- d_5

Figure 2. Key HMBC(H $\rightarrow$ C) and NOESY(H $\cdots$ H) correlations of compound **1**.

S9 UV Spectrum of Compound 2

MS Formula Results: - Scan (7.841 min) Sub (2011111403.d)

m/z	Ion	Formula	Abundance											
1215.5789	[M-H] ⁻	C59 H51 O26	400526.1											
Best	Formula (M)	Ion Formula	Calc. m/z	Score	Crises S	Mass	Calc. Mass	Diff (ppm)	Abs. Diff (ppm)	Abund. Match	Spacing Mat	Mass Match	m/z	DBE
x	[⁻	C59 H50 O26	C59 H51 O26	1215.5804	99.81	1216.580	1216.5877	-1.38	1.38	99.77	99.99	99.99	1215.5789	54
x	[⁻	C56 H48 O21	C56 H47 O21	1215.5343	99.22	1216.580	1216.5818	-3.45	3.45	99.02	99.99	99.99	1215.5789	23
x	[⁻	C77 H64 O13	C77 H63 O13	1215.5839	98.19	1216.580	1216.5912	4.27	4.27	94.82	99.99	99.99	1215.5789	38
x	[⁻	C64 H60 O8	C64 H59 O8	1215.578	97.72	1216.580	1216.5853	-0.56	0.56	92.04	99.99	99.99	1215.5789	45
x	[⁻	C73 H64 O16	C73 H63 O16	1215.5867	97.71	1216.580	1216.5799	-8.27	8.27	96.27	99.99	97.46	1215.5789	32
x	[⁻	C70 H60 O16	C70 H57 O16	1215.5698	97.7	1216.580	1216.5971	9.09	9.09	97.06	99.99	96.94	1215.5789	37
x	[⁻	C61 H76 O3	C61 H75 O3	1215.5722	96.32	1216.580	1216.5794	-5.76	5.76	85.93	99.99	98.92	1215.5789	54

S10 HRESIMS Spectrum of Compound 2

S13 HSQC Spectrum of Compound **2** in Pyridine- d_5

S14 HMBC Spectrum of Compound **2** in Pyridine- d_5

S15 TOCSY Spectrum of Compound **2** in Pyridine- d_5

S16 NOESY Spectrum of Compound **2** in Pyridine- d_5

Figure 3. Key HMBC(H $\rightarrow$ C) and NOESY(H $\cdots$ H) correlations of compound **2**.