SUPPLEMENTARY MATERIAL

Two new diacetylene glycosides: bhutkesoside A and B from the roots of *Ligusticopsis wallichiana*

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Abstract:

Two new diacetylene glycosides, bhutkesoside A (**1**) and B (**2**), along with 10 known compounds, *i.e.*, faltarindiol (**3**), chlorogenic acid (**4**), 5-*O-p*-coumaroyl-quinic acid (**5**), 3,5-di-*O*-caffeoyl-quinic acid (**6**), 4-hydroxy-7-methoxy-phenylethanol (**7**), ferulic acid (**8**), dehydrodiconiferyl alcohol-4-*O*- β -D-glucopyranoside (**9**), 5,7-dihydroxy-2-methylchromone-7-*O*-rutinoside (**10**), schumannofioside B (**11**) and marmesinin (**12**) were isolated from the roots of *Ligusticopsis wallichiana* (DC) Pimenov & Kljuykov (Apiaceae), commonly known as “Bhutkesh” in Nepal. The structures were determined on the basis of spectroscopic data. Compounds **4** and **6** showed potent antioxidant activity on DPPH free radical scavenging assay.

Keywords: *Ligusticopsis wallichiana*; Apiaceae; Bhutkesh; bhutkesoside A; bhutkesoside B

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Figure S1. ^1H NMR spectrum of compound **1**, **2** and **3**.

Figure S2. ^{13}C NMR spectrum of compound **1**, **2** and **3**.

Figure S3. COSY spectrum of compound **1**.

Figure S4. HMBC spectrum of compound **1**.

Figure S5. COSY spectrum of compound 2.

Figure S6. HMBC spectrum of compound 2.

Figure S7. ^1H - ^1H COSY and HMBC correlations of **1** and **2**.

Table S1. ^1H and ^{13}C NMR spectroscopic data of compound **3**.

Pos	Compound 3 *	
	$\delta^1\text{H}$ (J in Hz)	$\delta^{13}\text{C}$
1a,b	5.47, dt (17.2, 1.5) 5.25, dt (10.4, 1.5)	117.3, CH ₂
2	5.94, ddd (5.2, 10.4, 17.2)	135.7, CH
3	4.93, brd (5.2)	63.4, CH
4		78.2, C
5		70.3, C
6		68.7, C
7		79.8, C
	5.20, brd (8.5)	58.5, CH
9	5.51, brdd (8.5, 10.6)	127.6, CH
10	5.61, ddd (1.2, 7.3, 10.6)	134.6, CH
11	2.1, dq (1.2, 7.3)	31.7, CH ₂
12	1.38, t like (7.3)	29.2, CH ₂
13	1.27-1.29, m	29.2, CH ₂
14	1.27-1.29, m	29.2, CH ₂
15	1.27-1.29, m	27.2, CH ₂
16	1.27-1.29, m	22.1, CH ₂
17	0.88, t (7.0)	14.0, CH ₃

* ^1H NMR 500 MHz, ^{13}C NMR 125 MHz, CDCl₃

Table S2. ^1H spectroscopic data of compound **4**, **5** and **6**.

Pos	Compound 4 [*]	Compound 5 ^{**}		Compound 6 [*]
	$\delta^1\text{H}$ (J in Hz)	$\delta^1\text{H}$ (J in Hz)	$\delta^{13}\text{C}$	$\delta^1\text{H}$ (J in Hz)
1			78.3, C	
2	2.01-2.03, m ^a	1.88-2.08, m	36.6, CH ₂ ^a	2.09-2.29, m
3	4.22, m	4.10, m	70.7, CH ^b	5.40, q (3.4)
4	3.81, dd (3.4, 9.8)	3.58(overlapped,	71.6, CH ^b	3.98, dd (3.4, 9.4)
5	5.30, dt, (9.8, 3.4)	5.20, dt (10.2, 5.2)	72.6, CH ^b	5.46, dt, (9.4, 4.8)
6	2.11-2.19, m ^a	1.88-2.08, m	39.0, CH ₂ ^a	2.09-2.29, m
7			175.7, C	
1'			125.2, C	
2'	7.05, brs	7.50, brd (8.5)	130.2, CH	7.11, d (1.5) ^a
3'		6.78, brd (8.5)	114.7, CH	
4'			159.8, C	
5'		6.78, brd (8.5)	114.7, CH	6.82, brd (8.5)
6'	6.99, brd (8.2)	7.50, brd (8.5)	130.2, CH	7.01, brd (8.5) ^b
7'	7.51, d (15.9)	7.53, d (15.9)	144.3, CH	7.58, d (15.9) ^d
8'	6.25, d (15.9)	6.35, d (15.9)	115.9, CH	6.42, d (15.9) ^c
9'			166.4, C	
1''				
2''				7.10, d (1.5) ^a
3''				
4''				
5''				6.82, brd (8.5)
6''				6.99, brd (8.5) ^b
7''				7.60, d (15.9) ^d
8''				6.31, d (15.9) ^c
9''				

^{a,b,c,d} assignments with same superscripts may be may be interchanged in the same column

^{*} ^1H NMR, 500 MHz, CD₃OD+D₂O ^{**} ^1H NMR 500 MHz, ^{13}C NMR 125 MHz, DMSO-*d*₆

Table S3. ^1H and ^{13}C NMR spectroscopic data of compound **7** and **8**.

Pos	Compound 7 *		Compound 8 **	
	$\delta^1\text{H}$ (J in Hz)	$\delta^{13}\text{C}$	$\delta^1\text{H}$ (J in Hz)	$\delta^{13}\text{C}$
1		130.9, C		125.8, C
2	7.12, d (8.5)	129.3, CH	7.27, d (2.1)	111.2, CH
3	6.76, d (8.5)	116.2, CH		149.1, C
4		158.4, C		147.9, C
5	6.76, d (8.5)	116.2, CH	6.80, d (8.5)	115.6, CH ^a
6	7.12, d (8.5)	129.3, CH	7.08, dd (2.1, 8.2)	122.8, CH
7	4.16, dd (3.9, 8.2)	85.9, CH	7.51, d (15.9)	144.6, CH
8	3.61, dd (8.2, 11.9)	67.7, CH ₂	6.36, d (15.9)	115.5, CH ^a
	3.48, dd (3.9, 11.9)			
9				168.1, C
OCH	3.22, s	56.8, OCH ₃	3.82, s	55.7, OCH ₃

^a assignments with same superscripts may be may be interchanged in the same column* ^1H , NMR, 500 MHz, ^{13}C NMR 125 MHz, CD₃OD, ** ^1H , NMR 500 MHz, ^{13}C NMR 125 MHz, DMSO-*d*₆

Table S4. ^1H and ^{13}C NMR spectroscopic data of compound **9**.

Compound 9[*]		
Pos	$\delta^1\text{H}$ (J in Hz)	$\delta^{13}\text{C}$
1		138.1, C
2	7.02, brs	112.2, CH ^a
3		150.9, C
4		147.1, C
5	7.13, d (8.2)	118.0, CH ^b
6	6.91, dd, (8.2, 1.8)	119.4, CH ^b
7	5.57, d (5.8)	88.8, CH
8	3.45-3.48, m	55.3, CH
9	3.85, dd (7.0, 12.8)	64.9, CH ₂ ^e
1'		132.7, C ^c
2'	6.94, brs	111.2, CH ^a
3'		145.5, C
4'		149.2, C
5'		130.0, C ^c
6'	6.94, brs	116.5, CH ^b
7'	6.53, d (15.9)	131.9, CH
8'	6.21, dd (5.8, 15.9)	127.6, CH
9'	4.19, dd (1.2, 5.8)	63.8, CH ₂ ^e
Glc		
1''	4.87, d (7.3)	102.7, CH
2''	3.45-3.48, m	74.9, CH
3''	3.45-3.48, m	77.8, CH ^d
4''	3.36-3.38, m	71.3, CH
5''	3.45-3.48, m	78.2, CH ^d
6''	3.76, dd (7.0, 11.2)	62.5, CH ₂ ^e
	3.68, d (3.6, 11.2)	
OCH₃	3.82, s	56.8, OCH ₃
OCH₃	3.87, s	56.7, OCH ₃

^{a,b,c,d,e} assignments with same superscripts may be may be interchanged in the same column

^{*} ^1H NMR 500 MHz, ^{13}C NMR 125 MHz, CD₃OD+D₂O

Table S5. ^1H and ^{13}C NMR spectroscopic data of compound **10** and **11**.

Pos.	Compound 10 [*]		Compound 11 [*]	
	$\delta^1\text{H}$ (J in Hz)	$\delta^{13}\text{C}$	$\delta^1\text{H}$ (J in Hz)	$\delta^{13}\text{C}$
2		170.2, C		170.9, C
3	6.09, s	109.3, CH	6.19, s	109.3, CH ^b
4		184.1, C		184.2, C
5		162.8, C ^c		161.7, C ^c
6	6.64, br s	102.3, CH ^a	6.67, d (2.1)	100.6, CH ^a
7		164.5, C ^c		163.7, C ^c
8	6.46, 1H, (d, 1.8)	95.9, CH	6.49, d (2.1)	96.1, CH
9		159.4, C ^c		159.1, C ^c
10		106.8, C		106.6, C
2-CH3	2.42, s	20.5, CH ₃	2.43, s	20.6, CH ₃
Glc				
1'	4.97, d (7.3)	101.6, CH ^a	5.19, d (7.3)	99.6, CH ^a
2'	3.58 , dd (7.3, 10.7)	72.1, CH	3.50-3.55, m	78.8, CH ^d
3'	3.65-3.71, m	77.2, CH ^d	3.69-3.73, m	78.2, CH ^d
4'	3.62-3.63, m	71.5, CH ^b	3.50-3.55, m	71.3, CH
5'	3.65-3.71, m	74.1, CH	3.69-3.73, m	78.3, CH ^d
6'	3.77-3.79, m	67.7, CH ₂	3.95, d (2.1, 12.6)	62.3, CH ₂
	4.03-4.05, m		3.76, d (5.5, 12.6)	
Rha/Api				
1''	4.69, d (1.5)	101.2, CH ^a	5.42, d (2.1)	108.9, CH ^b
2''	3.90 , dd (1.5, 3.4)	72.3, CH	4.01 , dd (2.1, 5.8)	78.1, CH ^d
3''	3.64 , dd (3.4, 9.5)	77.9, CH		80.5, C
4''	3.65-3.71, m	69.8, CH ^b	3.99, d (10.0)	75.3, CH ₂
5''	3.46-3.48, m	74.7, CH	3.60-3.63, m	65.8, CH ₂
6''	1.21, d (7.0)	17.9, CH ₃	3.70, brd (9.1)	

^{a,b,c,d} assignments with same superscripts may be may be interchanged in the same column

^{*} ^1H NMR 500 MHz, ^{13}C NMR 125 MHz CD₃OD

Table S6. ^1H and ^{13}C NMR spectroscopic data of compound **12**.

Compound 12[*]		
Pos	$\delta^1\text{H}$ (J in Hz)	$\delta^{13}\text{C}$
2		164.4, C
3	6.29, d (9.5)	111.7, CH
4	7.98, d (9.5)	147.3, CH
5	7.50, s	125.2, CH
6		127.6, C
7		165.4, C
8	6.81, s	98.3, CH ^a
9		156.2, C
10		114.2, C
2'	4.96, dd (9.1, 9.5)	91.8, CH
3'	3.45, dd (9.1, 18)	30.3, CH ₂
	3.36, dd (9.5, 18)	
4'		79.9, C
5'	1.40, s	22.7, CH ₃
6'	1.33, s	22.7, CH ₃
Glc		
1''	4.71, d (7.9)	98.0, CH ^a
2''	3.18, dd (7.9, 9.5)	74.5, CH
3''	3.38, dd (9.1, 9.5)	77.1, CH ^b
4''	3.38, dd (9.1, 9.5)	70.6, CH
5''	3.24, ddd (2.4, 4.8, 9.5)	76.8, CH ^b
6''	3.55, dd (4.8, 12.2)	61.4, CH ₂
	3.36, m	

^{a,b} assignments with same superscripts may be may be
interchanged in the same column

^{*} ^1H NMR 500 MHz, ^{13}C NMR 125 MHz CD₃OD