**Natural Products Research**

**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., falcarindiol (3), chlorogenic acid (4), 5-\textit{O}-\textit{p}-coumaroyl-quinic acid (5), 3,5-di-\textit{O}-caffeoyl-quinic acid (6), 4-hydroxy-7-methoxy-phenylethanol (7), ferulic acid (8), dehydrodiconiferyl alcohol-4-\textit{O}-\textit{β}-d-glucopyranoside (9), 5,7-dihydroxy-2-methylchromone-7-\textit{O}-rutinoside (10), schumanniofioside 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.** $^1$H NMR spectrum of compound 1, 2 and 3.

1. $^1$H NMR, 500 MHz, CD$_3$OD

2. $^1$H NMR, 500 MHz, CD$_3$OD

3. $^1$H NMR, 500 MHz, CDCl$_3$
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. $^1$H-$^1$H COSY and HMBC correlations of 1 and 2.
Table S1. $^1$H and $^{13}$C NMR spectroscopic data of compound 3.

| Pos | Compound 3$^*$ | $^1$H (J in Hz) | $^{13}$C  |
|-----|----------------|-----------------|---------|
| 1a,b| 5.47, dt (17.2, 1.5) | 117.3, CH$_2$ |
|     | 5.25, dt (10.4, 1.5) |
| 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   | 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$_3$ |

$^1$H NMR 500 MHz, $^{13}$C NMR 125 MHz, CDCl$_3$
Table S2. $^1$H spectroscopic data of compound 4, 5 and 6.

| Pos | Compound 4 | Compound 5 | Compound 6 |
|-----|------------|------------|------------|
|     | $\delta^1$H (J in Hz) | $\delta^1$H (J in Hz) | $\delta^{13}$C |
| 1   | 2.01-2.03, m$^a$ | 1.88-2.08, m | 78.3, C |
| 2   | 4.22, m      | 4.10, m    | 36.6, CH$_2$$^a$ |
| 3   | 3.81, dd (3.4, 9.8) | 3.58 (overlapped, | 70.7, CH$_b$ |
| 4   | 5.30, dt (9.8, 3.4) | 5.20, dt (10.2, 5.2) | 71.6, CH$_b$ |
| 5   | 2.11-2.19, m$^a$ | 1.88-2.08, m | 7.11, d (1.5)$^a$ |
| 6   | 7.05, brs    | 7.50, brd (8.5) | 130.2, CH |
| 7   | 6.78, brd (8.5) | 6.78, brd (8.5) | 114.7, CH |
| 1$'$| 175.7, C     | 6.82, brd (8.5) | 159.8, C |
| 2$'$| 7.50, brd (8.5) | 7.50, brd (8.5) | 114.7, CH |
| 3$'$| 6.78, brd (8.5) | 6.78, brd (8.5) | 130.2, CH |
| 4$'$| 7.53, d (15.9) | 7.53, d (15.9) | 144.3, CH |
| 5$'$| 6.25, d (15.9) | 6.35, d (15.9) | 115.9, CH |
| 6$'$| 166.4, C     | 7.10, d (1.5)$^a$ | |
| 7$'$| 6.82, brd (8.5) | 6.82, brd (8.5) | 6.99, brd (8.5)$^b$ |
| 8$'$| 6.99, brd (8.5) | 7.50, brd (8.5) | 6.99, brd (8.5)$^b$ |
| 9$'$| 7.60, d (15.9)$^d$ | 7.60, d (15.9)$^d$ | 6.31, d (15.9)$^c$ |

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

$^1$H NMR, 500 MHz, CD$_3$OD+D$_2$O $^{13}$H NMR 500 MHz, $^{13}$C NMR 125 MHz, DMSO-$d_6$
Table S3. $^1$H and $^{13}$C NMR spectroscopic data of compound 7 and 8.

| Pos | Compound 7 * |  | Compound 8 ** |  |
|-----|--------------|---|--------------|---|
|     | $\delta^1$H (J in Hz) | $\delta^{13}$C | $\delta^1$H (J in Hz) | $\delta^{13}$C |
| 1   | 7.12, d (8.5) | 130.9, C | 7.27, d (2.1) | 125.8, C |
| 2   | 6.76, d (8.5) | 129.3, CH | 7.27, d (2.1) | 111.2, CH |
| 3   | 158.4, C | 116.2, CH | 7.27, d (2.1) | 149.1, C |
| 4   | 6.76, d (8.5) | 116.2, CH | 6.80, d (8.5) | 115.6, CH$^a$ |
| 5   | 7.12, d (8.5) | 129.3, CH | 7.08, dd (2.1, 8.2) | 122.8, CH |
| 6   | 4.16, dd (3.9, 8.2) | 85.9, CH | 7.51, d (15.9) | 144.6, CH |
| 7   | 3.61, dd (8.2, 11.9) | 67.7, CH$_2$ | 6.36, d (15.9) | 115.5, CH$^a$ |
| 8   | 3.48, dd (3.9, 11.9) |  |  |  |
| 9   | OCH | 3.22, s | 56.8, OCH$_3$ | 3.82, s |
| OCH |  |  |  | 55.7, OCH$_3$ |

* Assignments with same superscripts may be interchanged in the same column.

$^1$H, NMR, 500 MHz, $^{13}$C NMR 125 MHz, CD$_3$OD, $^*$H, NMR 500 MHz, $^{13}$C NMR 125 MHz, DMSO-$d_6$. 
Table S4. $^1$H and $^{13}$C NMR spectroscopic data of compound 9.

| Pos | $\delta ^1$H (J in Hz) | $\delta ^{13}$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$|
|     | 3.68, d (3.6, 11.2)    |                |
| OCH$_3$ | 3.82, s               | 56.8, OCH$_3$ |
| OCH$_3$ | 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

$^1$H NMR 500 MHz, $^{13}$C NMR 125 MHz, CD$_3$OD+D$_2$O
Table S5. $^1$H and $^{13}$C NMR spectroscopic data of compound 10 and 11.

| Pos. | Compound 10* | Compound 11* |
|------|--------------|--------------|
|      | $\delta^1$H (J in Hz) | $\delta^{13}$C | $\delta^1$H (J in Hz) | $\delta^{13}$C |
| 2    | 170.2, C     |              | 170.9, C             |              |
| 3    | 6.09, s      | 109.3, CH    | 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

*$^1$H NMR 500 MHz, $^{13}$C NMR 125 MHz CD$_3$OD
Table S6. $^1$H and $^{13}$C NMR spectroscopic data of compound 12.

| Compound 12* | Pos | $\delta^1$H (J in Hz) | $\delta^{13}$C |
|--------------|-----|------------------------|---------------|
| 2            | 6.29, d (9.5) | 111.7, CH |
| 3            | 7.98, d (9.5) | 147.3, CH |
| 4            | 7.50, s       | 125.2, CH |
| 5            | 127.6, C      |             |
| 6            | 165.4, C      |             |
| 7            | 6.81, s       | 98.3, CH$^a$ |
| 8            | 156.2, C      |             |
| 9            | 91.8, CH      |             |
| 10           | 3.45, dd (9.1, 18) | 30.3, CH$_2$ |
|              | 3.36, dd (9.5, 18) | 79.9, C |
| 4            | 1.40, s       | 22.7, CH$_3$ |
| 5            | 1.33, s       | 22.7, CH$_3$ |
| Glc          | 4.71, d (7.9) | 98.0, CH$^a$ |
| 1$^\`$       | 3.18, dd (7.9, 9.5) | 74.5, CH |
| 2$^\`$      | 3.38, dd (9.1, 9.5) | 77.1, CH$^b$ |
| 3$^\`$      | 3.38, dd (9.1, 9.5) | 70.6, CH |
| 4$^\`$      | 3.24, ddd (2.4, 4.8, 9.5) | 76.8, CH$^b$ |
| 5$^\`$      | 3.55, dd (4.8,12.2) | 61.4, CH$_2$ |
| 6$^\`$      | 3.36, m       |             |

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

$^1$H NMR 500 MHz, $^{13}$C NMR 125 MHz CD$_3$OD