SUPPLEMENTARY MATERIAL

Benzophenone glycosides from the pericarps of Aquilaria yunnanensis S. C. Huang

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ABSTRACT
Two new benzophenone glycosides, aquilarisides A (1) and B (2), together with six known analogues (3–8) were isolated from the pericarps of Aquilaria yunnanensis S. C. Huang. Their structures were elucidated on the basis of 1D and 2D NMR and mass spectroscopic analyses, and the absolute configuration of compound 1 was determined by experimental and calculated electronic circular dichroism (ECD) spectra. Anti-inflammatory activities of all compounds 1–8 were evaluated for their inhibitory activities against lipopolysaccharide (LPS)-stimulated induced nitric oxide (NO) production in RAW 264.7 cells using the Griess assay. Compound 2 indicated a weak inhibition of NO production.

KEYWORDS
Aquilaria yunnanensis; aquilarisides A and B; benzophenone glycoside; anti-inflammatory; nitric oxide; Griess assay
Figure S1 HRESIMS spectrum of compound 1

Figure S2 IR spectrum of compound 1
Figure S3 \(^1\)H NMR spectrum of compound 1 (500 MHz, methanol-\(d_4\))

Figure S4 Enlarged (\(\delta\) 2.8-4.5) \(^1\)H NMR spectrum of compound 1 (500 MHz, methanol-\(d_4\))
Figure S5 Enlarged (δ 6.0-7.8) $^1$H NMR spectrum of compound 1 (500 MHz, methanol-$d_4$)

Figure S6 $^{13}$C NMR spectrum of compound 1 (125 MHz, methanol-$d_4$)
Figure S7 HMBC spectrum of compound 1 (500 MHz, methanol-$d_4$)

Figure S8 NOESY spectrum of compound 1 (500 MHz, methanol-$d_4$)
Figure S9 Experimental, calculated ECD spectra (in MeOH) of compound 1

Figure S10 HRESIMS spectrum of compound 2
Figure S11 IR spectrum of compound 2

Figure S12 $^1$H NMR spectrum of compound 2 (500 MHz, methanol-$d_4$)
Figure S13 $^{13}$C NMR spectrum of compound 2 (125 MHz, methanol-$d_4$)

Figure S14 HMBC spectrum of compound 2 (500 MHz, methanol-$d_4$)
Table S1: $^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectroscopic data ($\delta$ in ppm) of compounds 1 and 2 (in methanol-d$_4$)

| position | 1 $\delta_H$ mult. ($J$ in Hz) | $\delta_C$ | 2 $\delta_H$ mult. ($J$ in Hz) | $\delta_C$ |
|-----------|-----------------|---------|-----------------|---------|
| 1         | 158.2           |         | 109.6           |         |
| 2         | 107.1           |         | 157.9           |         |
| 3         | 165.7           |         | 6.25 d (2.0)    | 95.1    |
| 4         | 6.36 s          | 90.1    |                 |         |
| 4a        | 159.2           |         |                 |         |
| 5         | 6.73 s          | 103.2   | 6.08 d (2.0)    | 98.1    |
| 5a        | 158.2           |         |                 |         |
| 6         | 145.9           |         | 160.5           |         |
| 7         | 7.39 s          | 154.0   | 197.6           |         |
| 8         |                 | 107.9   |                 |         |
| 8a        |                 | 112.5   |                 |         |
| 9         |                 | 181.3   |                 |         |
| 9a        |                 | 104.3   |                 |         |
| 1'a       | 3.55 d (17.0)   | 32.3    |                 | 132.9   |
| 1'b       | 3.03 d (17.0)   |         |                 |         |
| 2'        | 122.8           |         | 7.62 d (8.5)    | 132.7   |
| 3'        | 4.21 d (2.5)    | 82.7    | 6.84 d (8.5)    | 116.2   |
| 4'        | 4.03 m          | 78.7    |                 | 163.4   |
| 5'        | 4.09 m          | 86.2    | 6.84 d (8.5)    | 116.2   |
| 6'a       | 3.77 m          | 62.8    | 7.62 d (8.5)    | 132.7   |
| 6'b       | 3.67 m          |         |                 |         |
| 1''       |                 | 5.29 s  | 99.8            |         |
| 2''       |                 | 3.51 m  | 71.5            |         |
| 3''       |                 | 3.13 dd (9.5,3.0) | 69.8 |
| 4''       |                 | 4.86 m  | 75.0            |         |
| 5''       |                 | 3.51 m  | 68.7            |         |
| 6''       |                 | 1.09 d (6.0) | 17.9   |
| 1'''      |                 |         | 172.2           |         |
| 2'''      |                 | 2.72 s  | 46.3            |         |
| 3'''      |                 |         | 70.9            |         |
| 4'''      |                 | 2.69 d (4.5) | 45.9   |
| 5'''      |                 |         | 173.2           |         |
| 6'''      |                 | 1.38 s  | 28.0            |         |
| 7'''      |                 | 3.67 s  | 52.0            |         |
Table S2 $^1$H and $^{13}$C NMR spectroscopic data ($\delta$ in ppm) of iriflophenone 2-$O$-$\alpha$-$L$-[4$''$-$O$-$[3''''(S)-hydroxy-methylglutaryl]]-rhamnopyranoside and compound 3

| Position | $\delta$H mult. ($J$ in Hz) | $\delta$C | $\delta$H mult. ($J$ in Hz) | $\delta$C |
|----------|-----------------------------|-----------|-----------------------------|-----------|
| 1        | 108.1                       | 109.5     |                             |           |
| 2        | 156.5                       | 158.0     |                             |           |
| 3        | 6.25 d (2.0)                | 6.25 d (2.0) | 93.6                       | 95.0      |
| 4        | 161.5                       | 163.0     |                             |           |
| 5        | 6.08 d (2.0)                | 6.09 d (2.0) | 96.6                       | 98.1      |
| 6        | 159.1                       | 160.6     |                             |           |
| 7        | 196.2                       | 197.7     |                             |           |
| 1'       | 131.5                       | 132.9     |                             |           |
| 2',6'    | 7.61 d (8.8)                | 7.61 d (8.5) | 131.2                       | 132.6     |
| 3',5'    | 6.84 d (8.8)                | 6.86 d (8.5) | 114.8                       | 116.2     |
| 4'       | 161.9                       | 163.4     |                             |           |
| 1''      | 5.28 d (1.6)                | 5.28 d (1.6) | 98.3                       | 99.7      |
| 2''      | 3.51 m                      | 3.52 m    | 70.1                        | 71.5      |
| 3''      | 3.11 dd (9.8,3.4)           | 68.4      | 3.09 dd (9.5,3.0)           | 69.8      |
| 4''      | 4.84 m                      | 4.84 m    | 73.6                        | 75.1      |
| 5''      | 3.51 m                      | 3.49 m    | 67.3                        | 68.7      |
| 6''      | 1.08 d (6.2)                | 1.09 d (6.0) | 16.5                       | 17.9      |
| 1'''     | 170.9                       |           |                             |           |
| 2'''     | 2.72 s                      | 2.68 s    | 44.9                        | 46.9      |
| 3'''     |                             | 69.4      |                             |           |
| 4'''     | 2.63 d (15.2)               | 2.53 d (15.0) | 44.4                       | 46.7      |
| 5'''     | 2.68 d (15.2)               | 2.61 d (15.0) | 173.3                       | 173.8     |
| 6'''     | 1.39 s                      | 1.37 s    | 26.5                        | 27.9      |
Table S3 $^1$H and $^{13}$C NMR spectroscopic data ($\delta$ in ppm) of iriflophenone 2-\(O\)-\(\beta\)-D-xylopyranoside and compound 4

| position | iriflophenone 2-\(O\)-\(\beta\)-D-xylopyranoside (500 and 125 MHz, methanol-\(d_4\)) | 4 (500 and 125 MHz, methanol-\(d_4\)) |
|----------|--------------------------------|---------------------------------|
|          | $\delta$H mult. (J in Hz) | $\delta$C | $\delta$H mult. (J in Hz) | $\delta$C |
| 1        | 108.7 | 110.0 |
| 2        | 157.2 | 158.7 |
| 3        | 6.17 d (2.0) | 94.3 | 6.16 d (2.0) | 95.8 |
| 4        | 161.2 | 163.1 |
| 5        | 6.06 d (2.0) | 96.8 | 6.06 d (2.0) | 98.3 |
| 6        | 158.6 | 160.2 |
| 7        | 196.0 | 197.4 |
| 1'       | 130.9 | 132.3 |
| 2',6'    | 7.65 d (8.8) | 131.9 | 7.65 d (8.0) | 133.4 |
| 3',5'    | 6.78 d (8.8) | 114.3 | 6.77 d (8.0) | 115.8 |
| 4'       | 162.1 | 163.8 |
| 1''      | 4.79 d (7.3) | 101.2 | 4.79 d (7.5) | 102.6 |
| 2''      | 3.04 dd (8.9,7.3) | 73.0 | 3.04 m | 74.4 |
| 3''      | 3.30 m | 75.9 | 3.30 m | 77.4 |
| 4''      | 3.44 m | 69.4 | 3.43 m | 70.8 |
| 5''      | 3.27 dd (11.4,9.8) | 65.4 | 3.26 m | 66.9 |
|          | 3.85 dd (11.4,5.2) | 3.85 dd (11.5,5.0) |
Table S4 \(^1\)H and \(^{13}\)C NMR spectroscopic data (δ in ppm) of iriflophenone 2-\(\alpha\)-\(\text{L}\)-rhamnoside and compound 5

| position | \(\delta_\text{H}\) mult. (\(J\) in Hz) | \(\delta_\text{C}\) | \(\delta_\text{H}\) mult. (\(J\) in Hz) | \(\delta_\text{C}\) |
|----------|---------------------------------|-----------------|---------------------------------|-----------------|
| 1        | 109.6                           |                 | 109.5                           |                 |
| 2        | 160.5                           |                 | 158.4                           |                 |
| 3        | 6.34 d (2.0)                    | 95.6            | 6.29 d (2.0)                    | 95.7            |
| 4        | 163.4                           |                 | 163.5                           |                 |
| 5        | 6.11 d (2.0)                    | 98.0            | 6.07 d (2.0)                    | 98.1            |
| 6        | 158.4                           |                 | 158.4                           |                 |
| 7        | 197.6                           |                 | 197.6                           |                 |
| 1\(^{\prime}\) | 128.8                        |                 | 130.9                           |                 |
| 2\(^{\prime}\),6\(^{\prime}\) | 7.65 d (8.5)                     | 132.7          | 7.61 d (8.5)                    | 132.7          |
| 3\(^{\prime}\),5\(^{\prime}\) | 6.85 d (8.5)                        | 116.1          | 6.81 d (8.5)                    | 116.1          |
| 4\(^{\prime}\) | 163.0                        |                 | 163.3                           |                 |
| 1\(^{\prime\prime}\) | 5.26 d (1.0)                     | 100.5          | 5.22 d (1.0)                    | 100.5          |
| 2\(^{\prime\prime}\) | 3.45-3.50 m                     | 71.6            | 3.43 m                          | 71.6            |
| 3\(^{\prime\prime}\) | 3.16 dd (9.5,3.0)                 | 71.9            | 3.12 dd (9.5,3.5)               | 71.9            |
| 4\(^{\prime\prime}\) | 3.32 dd (9.5,3.0)                 | 73.6            | 3.28 dd (9.5,3.5)               | 73.6            |
| 5\(^{\prime\prime}\) | 3.45-3.50 m                     | 70.8            | 3.40 m                          | 70.8            |
| 6\(^{\prime\prime}\) | 1.23 d (6.0)                     | 18.0            | 1.19 d (6.0)                    | 18.0            |
Table S5 $^1$H and $^{13}$C NMR spectroscopic data ($\delta$ in ppm) of iriflophenone 2-O-β-D-glucopyranoside and compound 6

| Position | $\delta_H$ (in ppm) | Mult. (J in Hz) | $\delta_C$ (in ppm) | $\delta_H$ (in ppm) | Mult. (J in Hz) | $\delta_C$ (in ppm) |
|----------|----------------------|-----------------|---------------------|----------------------|-----------------|---------------------|
| 1        | 110.3                |                 |                     | 110.2                |                 |                     |
| 2        | 158.7                |                 |                     | 158.8                |                 |                     |
| 3        | 6.24 d (1.8)         | 95.8            | 6.24 d (1.8)        | 96.0                 |                 |                     |
| 4        | 162.4                |                 | 98.1                | 6.06 d (1.8)         | 162.9           |                     |
| 5        | 159.6                |                 | 197.5               | 159.9                |                 |                     |
| 6        | 7                    | 132.1           | 133.5               | 7.68 d (8.8)         | 132.2           |                     |
| 1'       | 132.1                |                 |                     | 7.67 d (8.4)         | 133.5           |                     |
| 2',6'    | 6.78 d (8.8)         | 115.8           | 6.78 d (8.4)        | 115.9                |                 |                     |
| 3',5'    | 163.6                |                 |                     | 163.9                |                 |                     |
| 4'       | 163.6                |                 |                     | 163.9                |                 |                     |
| 1''      | 4.82 d (7.6)         | 102.2           | 4.82 d (7.8)        | 102.3                |                 |                     |
| 2''      | 3.09 dd (8.8,7.6)    | 74.6            | 3.08 t (9.0)        | 74.7                 |                 |                     |
| 3''      | 3.37 dd (9.3,8.8)    | 77.7            | 3.36 m              | 77.8                 |                 |                     |
| 4''      | 3.27 t (9.3)         | 71.0            | 3.27 t (9.6)        | 71.1                 |                 |                     |
| 5''      | 3.33-3.37 m          | 78.1            | 3.35 m              | 78.2                 |                 |                     |
| 6''      | 3.67 dd (12.3,5.3)   | 62.4            | 3.86 dd (12.0,5.4)  | 62.5                 |                 |                     |
|          | 3.67 dd (12.3,5.3)   |                 |                     |                      |                 |                     |
| Position | 1H mult. (J in Hz) | 13C | 1H mult. (J in Hz) | 13C |
|----------|-------------------|-----|-------------------|-----|
| 1        | 6.25 d (2.0)      | 95.1| 6.22 d (2.0)      | 94.9|
| 2        |                   | 158.0|                   | 157.8|
| 3        | 6.08 d (2.0)      | 98.1| 6.06 d (2.0)      | 97.9|
| 4        |                   | 160.6|                   | 160.3|
| 5        |                   | 197.7|                   | 197.6|
| 6        |                   | 133.1|                   | 132.8|
| 7        |                   | 7.60 d (8.7) | 132.8| 7.60 d (8.5) | 132.7|
| 8        |                   | 6.80 d (8.7) | 116.3| 6.81 d (8.5) | 116.1|
| 9        |                   | 163.1|                   | 163.4|
| 10       | 5.29 d (1.4)      | 99.8| 5.26 d (1.4)      | 99.6|
| 11       | 3.52 m            | 71.6| 3.49 m            | 71.5|
| 12       | 3.09 m            | 69.9| 3.07 m            | 69.7|
| 13       | 3.79 m            | 79.2| 4.78 m            | 75.0|
| 14       | 3.48 m            | 68.8| 3.45 m            | 68.7|
| 15       | 1.05 d (6.0)      | 17.9| 1.03 d (6.0)      | 17.8|
| 16       | 2.0 s             | 21.1| 2.0 s             | 21.0|
| 17       |                   | 172.7|                   | 172.5|
### Table S7

| Position | $\delta_H$ | mult. ($J$ in Hz) | $\delta_C$ | $\delta_H$ | mult. ($J$ in Hz) | $\delta_C$ |
|----------|------------|-------------------|------------|------------|-------------------|------------|
| 1        | 1.079      |                   | 109.2      |            |                   |            |
| 2        | 156.6      |                   | 158.1      |            |                   |            |
| 3        | 6.23 d (1.9)| 93.5              | 6.23 d (1.5)| 95.0      |                   |            |
| 4        | 161.9      |                   | 163.5      |            |                   |            |
| 5        | 6.07 d (1.9)| 96.6              | 6.07 d (1.5)| 98.1      |                   |            |
| 6        | 159.3      |                   | 160.9      |            |                   |            |
| 7        | 196.3      |                   | 197.7      |            |                   |            |
| 1'       | 131.7      |                   | 133.0      |            |                   |            |
| 2',6'    | 7.58 d (8.7)| 131.1             | 7.58 d (9.0)| 132.5     |                   |            |
| 3',5'    | 6.81 d (8.7)| 115.1             | 6.81 d (8.5)| 116.3     |                   |            |
| 4'       | 161.7      |                   | 163.5      |            |                   |            |
| 1''      | 5.27 br s (d, 1.4)$^a$| 98.2             | 5.27 br s  | 99.7      |                   |            |
| 2''      | 3.51 m     |                   | 70.0       | 71.4      |                   |            |
| 3''      | 3.02 dd (9.8,3.4)| 68.3             | 3.03 dd (9.5,3.0)| 69.7    |                   |            |
| 4''      | 4.86 m     |                   | 74.5       | 75.9      |                   |            |
| 5''      | 3.48 m     |                   | 67.2       | 68.7      |                   |            |
| 6''      | 1.08 d (6.2)| 16.3              | 1.09 d (6.0)| 17.8      |                   |            |
| 1'''     | 168.0      |                   | 169.4      |            |                   |            |
| 2'''     | 4.02 d (15.7)$^a$| 45.8$^a$           | 4.11 d (15.7)$^a$| 193.7  | 193.7              |            |
| 3'''     | 192.3      |                   |            |            |                   |            |
| 4'''     | 127.7      |                   |            |            |                   |            |
| 5'''     | 7.89 d (8.7)| 131.1             | 7.90 d (8.5)| 132.5     |                   |            |
| 6'''     | 6.87 d (8.7)| 114.8             | 6.86 d (8.5)| 116.6     |                   |            |
| 7'''     | 163.1      |                   | 165.0      |            |                   |            |
| 8'''     | 6.87 d (8.7)| 114.8             | 6.86 d (8.5)| 116.6     |                   |            |
| 9'''     | 7.89 d (8.7)| 131.1             | 7.90 d (8.5)| 132.5     |                   |            |

Note: $^a$Observed in acetonitrile-$d_3$
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