Supporting Information

Soluble Epoxide Hydrolase Inhibitory and Anti-inflammatory Components from the Leaves of *Eucommia ulmoides* Oliver (Duzhong)

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Quercetin (**1**): $C_{15}H_{10}O_7$, yellow powder; UV (MeOH) λ_{max} 257, 373 nm; ^{13}C-NMR see Table 1, ^{1}H-NMR see Table 2; ESI-MS *m/z*: 301.14 $[M-H]^-$.

Quercetin 3-glucoside (**2**): $C_{21}H_{20}O_{12}$, yellow powder; UV (MeOH) λ_{max} 260, 358 nm; ^{13}C-NMR see Table 1, ^{1}H-NMR see Table 2; ESI-MS *m/z*: 463.27 $[M-H]^-$.

Quercetin 3-rutinoside (**3**): $C_{27}H_{30}O_{16}$, yellow powder; UV (MeOH) λ_{max} 260, 359 nm; ^{13}C-NMR see Table 1, ^{1}H-NMR see Table 2; ESI-MS *m/z*: 633.22 $[M+Na]^+$.

Quercetin 3-sambubioside (**4**): $C_{26}H_{28}O_{16}$, yellow powder; UV (MeOH) λ_{max} 259, 358 nm; ESI-MS *m/z*: 619.13 $[M+Na]^+$; ^{13}C-NMR see Table 1, ^{1}H-NMR see Table 2.

Kaempferol (**5**): $C_{15}H_{10}O_6$, yellow powder; UV (MeOH) λ_{max} 266, 364 nm; ^{13}C-NMR see Table 1, ^{1}H-NM Rsee Table 2; ESI-MS *m/z*: 285.36 $[M-H]^-$.

Kaempferol 3-glucoside (**6**): $C_{21}H_{20}O_{11}$, yellow powder; UV (MeOH) λ_{max} 263, 347 nm; ^{13}C-NMR see Table 1, ^{1}H-NMR see Table 2; ESI-MS *m/z*: 447.35 $[M-H]^-$.

Kaempferol 3-rutinoside (**7**): $C_{27}H_{30}O_{15}$, yellow powder; UV (MeOH) λ_{max} 267, 352 nm; ^{13}C-NMR see Table 1, ^{1}H-NMR see Table 2; ESI-MS *m/z*: 617.34 $[M+Na]^+$.

Table 1. ^{13}C NMR data of compounds **1-7** (MeOH-d_4).

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
2	146.7	158.5	158.5	158.3	148.0	158.5	161.2
3	135.7	135.6	135.6	135.2	137.1	135.3	135.5
4	175.8	179.5	179.4	179.6	177.3	179.5	179.4
5	160.7	163.1	162.9	163.2	162.5	163.0	162.9
6	98.2	99.9	100.0	99.7	99.3	99.9	100.0
7	164.0	166.0	166.1	165.8	165.7	166.1	166.1
8	93.3	94.7	94.9	94.6	94.5	94.8	95.0
9	156.1	159.1	159.3	158.4	158.2	159.1	158.5
10	102.9	105.7	105.6	105.8	104.5	105.7	105.6
1'	121.9	123.2	123.1	123.3	123.7	122.8	122.7
2'	115.0	117.6	117.7	117.3	130.7	132.3	132.4
3'	145.0	145.9	145.8	146.0	116.3	116.1	116.1
4'	147.6	149.9	149.8	149.7	160.5	161.5	159.4

5'	115.6	116.0	116.1	116.1	116.3	116.1	116.1
6'	120.0	123.1	123.6	123.4	130.7	132.3	132.4
1"		104.3	104.7	100.9		104.2	104.4
2"		75.2	75.7	82.3		75.7	75.8
3"		78.1	78.2	78.2		78.0	78.1
4"		71.2	71.4	71.1		71.4	71.4
5"		78.4	77.2	77.0		78.4	77.2
6"		62.6	68.5	62.4		62.6	68.6
1"'			102.4	105.3			102.4
2"'			72.1	74.9			72.1
3"'			72.2	78.3			72.3
4"'			73.9	71.0			73.9
5"'			69.7	66.6			69.7
6"'			17.9				17.9

Table 2. ^{1}H NMR data of compounds **1-7** (MeOH-d_4).

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
6	6.40, d, 1.4	6.22, d, 2.0	6.21, d, 1.7	6.25, d, 2.0	6.19, d, 1.3	6.21, s	6.20, br
8	6.18, d, 1.4	6.41, d, 1.7	6.43, d, 1.5	6.41, d, 2.0	6.40, d, 1.3	6.40, s	6.39, br
2'	7.68, d, 1.8	7.73, d, 2.1	7.71, d, 1.7	7.67, m	8.09, d, 8.6	8.06, d, 8.6	8.06, d, 8.2
3'					6.92, d, 8.8	6.90, d, 8.7	6.89, d, 8.3
5'	6.88, d, 8.5	6.89, d, 8.5	6.87 d, 8.4	6.90 d, 8.2	6.92, d, 8.8	6.90, d, 8.7	6.89, d, 8.3
6'	7.54, dd, 8.5, 1.9	7.60, dd, 8.5, 2.1	7.64, dd, 8.5, 1.8	7.67, m	8.09, d, 8.6	8.06, d, 8.6	8.06, d, 8.2
1"		5.27, d, 7.6	5.08, d, 7.6	5.51, d, 7.5		5.25, d, 7.1	5.12, d, 6.2
1'"			4.53, s	4.81, d, 7.0			4.52, s

Catechin-(7,8-bc)-4α-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranone (**8**): $C_{24}H_{20}O_9$, colorless solid; $[\alpha]_D^{21.4}$ -134.2; UV (MeOH) λ_{max} 207, 283 nm; ESI-MS *m/z*: 451.11 $[M-H]^-$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 82.8 (C-2), 68.2 (C-3), 28.1 (C-4), 105.7 (C-4a), 156.9 (C-5), 96.3 (C-6), 153.0 (C-7), 105.9 (C-8), 152.2 (C-8a), 131.7 (C-1'), 115.1 (C-2'), 145.2 (C-3'), 146.0 (C-4'), 116.0 (C-5'), 119.6 (C-6'), 38.6 (C-α), 35.4 (C-β), 135.4 (C-1"), 114.8 (C-2"), 146.1 (C-3"), 146.3 (C-4"), 116.5 (C-5"), 119.5 (C-6"), 170.6 (-COO-).^{1}H NMR (500 MHz, MeOH-d_4) δ 4.69 (1H, d, J = 6.9 Hz, H-2), 3.96 (1H, m, H-3), 2.59 (1H, dd, J = 16.0, 7.5 Hz, H-4α), 3.02 (1H, dd, J = 15.8, 7.2 Hz, H-4β), 6.20 (1H, s, H-6), 6.64 (1H, d, J = 1.9 Hz, H-2'), 6.66 (1H, d, J = 8.1 Hz, H-5'), 6.44 (1H, dd, J = 8.2, 2.1 Hz, H-6'), 2.81 (2H, m, H-α×2), 4.39 (1H, d, J = 6.3 Hz, H-β), 6.52 (1H, d, J = 2.1 Hz, H-2"), 6.58 (1H, d, J = 8.2 Hz, H-5"), 6.38 (1H, dd, J = 8.2, 1.9 Hz, H-6").

Catechin-(5, 6-bc)-4α-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranone and Catechin-(5, 6-bc)-4β-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranone **(9)**: $C_{24}H_{20}O_9$, colorless solid; UV (MeOH) λ_{max} 229, 283 nm; ESI-MS *m/z*: 451.08 $[M-H]^-$; ^{13}C signals could be devided into two groups according to their relative heights and they were assigned as follows:

Catechin-(5, 6-bc)-4α-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranone

^{13}C NMR (125 MHz, MeOH-d_4) δ 82.9 (C-2), 68.1 (C-3), 27.7 (C-4), 101.4 (C-4a), 151.8 (C-5), 107.2 (C-6), 154.8 (C-7), 99.8 (C-8), 155.8 (C-8a), 131.9 (C-1'), 115.0

(C-2'), 145.2 (C-3'), 146.3 (C-4', 3", 4"), 116.2 (C-5'), 119.8 (C-6'), 38.4 (C-α), 35.2 (C-β), 134.9 (C-1"), 115.1 (C-2"), 116.5 (C-5"), 119.3 (C-6"), 170.3 (-COO-).

Catechin-(5, 6-bc)-4β-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranone

^{13}C NMR (125 MHz, MeOH-d_4) δ 82.8 (C-2), 68.1 (C-3), 27.8 (C-4), 101.5 (C-4a), 151.9 (C-5), 107.2 (C-6), 154.8 (C-7), 99.8 (C-8), 155.8 (C-8a), 131.8 (C-1'), 115.0 (C-2'), 145.2 (C-3'), 146.3 (C-4', 3", 4"), 116.2 (C-5'), 119.7 (C-6'), 38.3 (C-α), 35.2 (C-β), 134.9 (C-1"), 115.0 (C-2"), 116.5 (C-5"), 119.2 (C-6"), 170.3 (-COO-); ^{1}H NMR (500 MHz, MeOH-d_4) δ 4.72 (1H, d, *J* = 7.0 Hz, H-2), 4.09 (1H, m, H-3), 2.71 (1H, dd, *J* = 16.4, 7.5 Hz, H-4α), 2.97 (1H, dd, *J* = 16.4, 5.2 Hz, H-4β), 6.23 (1H, s, H-8), 6.85 (1H, d, *J* = 1.9 Hz, H-2'), 6.80 (1H, d, *J* = 8.1 Hz, H-5'), 6.74 (1H, dd, *J* = 8.0, 1.9 Hz, H-6'), 3.04 (1H, m, H-α), 2.89 (1H, m, H-α), 4.47 (1H, d, *J* = 6.6 Hz, H-β), 6.58 (1H, d, *J* = 2.1 Hz, H-2"), 6.69 (1H, d, *J* = 8.1 Hz, H-5"), 6.49 (1H, dd, *J* = 8.2, 2.1 Hz, H-6").

Syringin (**10**): $C_{17}H_{24}O_9$, white powder; UV (MeOH) λ_{max} 229, 267 nm; ESI-MS *m/z*: 395.14 $[M+Na]^+$; ^{13}C NMR (100 MHz, MeOH-d_4) δ 135.2 (C-1), 105.4 (C-2, 6), 154.3 (C-3, 5), 135.8 (C-4), 130.0 (C-7), 131.3 (C-8), 63.6 (C-9), 105.3 (C-1'), 75.7 (C-2'), 78.3 (C-3'), 71.3 (C-4'), 77.8 (C-5'), 62.5 (C-6'), 57.0 (OCH_3-3, 5). ^{1}H NMR (400 M Hz, MeOH-d_4) δ 6.78 (2H, s, H-2, 6), 6.57 (1H, d, *J* = 15.9 Hz, H-7), 6.35 (1H, dt, *J* = 15.8, 5.6 Hz, H-8), 4.25 (2H, dd, *J* = 5.6, 1.5 Hz, H-9), 4.89 (1H, d, *J* = 7.5 Hz, Glc H-1'), 3.18-3.45 (4H, m, H-2', 3', 4', 5'), 3.76 (1H, dd, *J* = 12.0, 2.4 Hz, H-6'), 3.64 (1H, dd, *J* = 12.0, 5.1 Hz, H-6'), 3.89 (6H, s, OCH_3×2).

2,5-dimethoxy-3-glucopyranosyl cinnamic alcohol (**11**): $C_{17}H_{24}O_9$, colorless solid; UV (MeOH) λ_{max} 229, 267 nm; ESI-MS *m/z*: 395.24 $[M+Na]^+$; ^{13}C NMR (125 MHz, DMSO) δ 152.7 (C-1, C-4), 104.5 (C-2, C-6), 133.9 (C-3), 132.6 (C-5), 128.4 (C-7), 130.2 (C-8), 61.4 (C-9), 102.6 (C-1'), 77.2 (C-2'), 76.5 (C-3'), 70.0 (C-4'), 74.2 (C-5'), 60.9 (C-6'), 56.4 (2×OCH_3). ^{1}H NMR (500 MHz, DMSO) δ 6.73 (2H, s, H-2, H-6), 6.47 (1H, d, *J* = 15.9 Hz, H-7), 6.34 (1H, dt, *J* = 15.9, 5.0 Hz, H-8), 4.11 (2H, m, H-9), 4.91 (1H, d, *J* = 7.0 Hz, H-1'), 3.04-3.60 (6H, m, H-2'-H-6'), 3.77 (6H, s, 2×OCH_3).

Methyl-caffeate (**12**): $C_{10}H_{10}O_4$, pale needle; UV (MeOH) λ_{max} 243, 298 nm; ESI-MS *m/z*: 193.02 $[M-H]^-$, ^{13}C NMR (125 MHz, MeOH-d_4) δ127.7 (C-1), 116.5 (C-2), 146.9 (C-3), 149.6 (C-4), 115.1 (C-5), 122.9 (C-6), 146.8 (C-7), 114.8 (C-8), 52.0 (OCH_3)

169.8 (CO). ^{1}H NMR (500 MHz, MeOH-d_4) δ 7.05 (1H, d, J = 2.0 Hz, H-2), 6.80 (1H, d, J = 8.2 Hz, H-5), 6.96 (1H, d, J = 8.2 Hz, H-6), 7.56 (1H, d, J = 15.9 Hz, H-7), 6.28 (1H, d, J = 15.9 Hz, H-8), 3.77 (3H, s, CH_3).

erythro-Guaiacylglycerole (**13**): $C_{10}H_{14}O_5$, colorless amorphous powder; UV (MeOH) λ_{max} 229, 281 nm; ESI-MS *m/z*: 237.02 $[M+Na]^+$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 134.8 (C-1), 111.5 (C-2), 148.9 (C-3), 147.1 (C-4), 115.9 (C-5), 120.7 (C-6), 75.5 (C-7), 77.6 (C-8), 64.2 (C-9), 56.3 (O<u>C</u>H$_3$); ^{1}H NMR (500 MHz, MeOH-d_4) δ 7.01 (1H, d, J = 1.4 Hz, H-2), 6.78 (1H, d, J = 8.0 Hz, H-5), 6.2 (1H, m, H-6), 4.53 (1H, d, J = 6.3 Hz, H-7), 3.68 (1H, td, J = 6.2, 3.9 Hz, H-8), 3.49 (1H, dd, J = 11.3, 3.8 Hz, H-9a), 3.37 (1H, dd, J = 11.2, 6.5 Hz, H-9b), 3.87 (3H, s, OCH_3).

Methyl-chlorogenate (**14**): $C_{17}H_{20}O_9$, white powder; UV (MeOH) λ_{max} 330 nm; ESI-MS *m/z*: 367.05 $[M-H]^-$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 127.6 (C-1), 115.0 (C-2), 146.8 (C-3), 149.7 (C-4), 116.5 (C-5), 123.0 (C-6), 72.1 (C-1'), 72.6 (C-2'), 70.3 (C-3'), 38.0 (C-4', 6'), 75.8 (C-5'), 175.4 (C-7'), 53.0 (C-8'), 147.2 (C-α), 115.1 (C-β), 168.3 (C-γ); ^{1}H NMR (500 MHz, MeOH-d_4) δ7.05 (1H, d, J = 1.9 Hz, H-2), 6.95 (1H, dd, J = 8.2, 1.9 Hz, H-3), 6.79 (1H, d, J = 8.2 Hz, H-5), 6.22 (1H, d, J = 15.9 Hz, H-α), 7.53 (1H, d, J = 15.9 Hz, H-β), 5.29 (1H, td, J = 7.6, 4.4 Hz, H-1'), 4.14 (1H, dt, J = 6.5, 3.2 Hz, H-2'), 3.74 (1H, dd, J = 7.4, 3.0 Hz, H-3'), 2.24 – 2.10 (3H, m, H-4', 6'a), 2.02 (1H, dd, J = 13.5, 6.6 Hz, H-6'b), 3.70 (3H, s, H-OMe).

Sinenoside I (**15**): $C_{26}H_{34}O_{12}$, white crystal; $[\alpha]_D^{21.9}$ -43.75; UV (MeOH) λ_{max} 229, 279 nm;, ESI-MS *m/z*: 537.89 $[M-H]^-$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 135.2 (C-1), 111.6 (C-2), 149.1 (C-3), 147.4 (C-4), 115.8 (C-5), 120.8 (C-6), 85.8 (C-7), 62.0 (C-8), 60.7 (C-9), 56.4 (3-OCH_3), 134.1 (C-1'), 116.2 (C-2'), 146.7 (C-3'), 150.3 (C-4'), 117.8 (C-5'), 124.0 (C-6'), 82.5 (C-8'), 40.7 (C-7'), 77.9 (C-9'), 56.7 (3'-OCH_3), 103.0 (C-1''), 74.9 (C-2''), 77.8 (C-3''), 71.4 (C-4''), 78.2 (C-5''), 62.5 (C-6''). ^{1}H NMR (500 MHz, MeOH-d_4) δ 7.17 (1H, d, J = 1.9 Hz, H-2), 6.78 (1H, d, J = 8.1 Hz, H-5), 6.91 (1H, dd, J = 8.2, 1.9 Hz, H-6), 4.76 (1H, d, J = 7.3 Hz, H-7), 2.34 (1H, dd, J = 12.9, 6.2 Hz, H-8), 7.04 (1H, d, J = 1.9 Hz, H-2'), 7.13 (1H, d, J = 8.3 Hz, H-5'), 6.88 (1H, dd, J = 8.3, 1.9 Hz, H-6'), 3.07 (1H, d, J = 13.9 Hz, H-7'a), 3.00 (1H, d, J = 13.9 Hz, H-7'b), 3.86 (1H, m, H-9'a), 3.84 (1H, m, H-9'b), 4.91 (1H, d, J = 7.5 Hz, H-1''), 3.90 (4H, m, H-9a, 3-OCH_3), 3.89 (4H, m, H-9b, 3'-OCH_3).

Liriodendrin (**16**): $C_{34}H_{46}O_{18}$, white powder; $[\alpha]_D^{23.5}$ -15.9; UV (MeOH) λ_{max} 229 nm; ESI-MS *m/z*: 741.29 $[M-H]^-$; ^{13}C NMR (125 MHz, DMSO) δ53.6 (C-1, 5), 85.0 (C-2, 6), 71.3 (C-4, 8), 152.6 (C-3', 5', 3''', 5'''), 133.8 (C-1', 1'''), 104.2 (C-6''', 6', 2''', 2'), 137.1 (C-4', 4'''), 77.2 (C-5'', 5''''), 102.7 (C-1'', 1''''), 74.2 (C-2'', 2''''), 76.5 (C-3'', 3''''), 69.9 (C-4'', 4''''), 60.9 (C-6'', 6''''), 56.4 (C-3', 5', 3''', 5'''-OCH_3). ^1H NMR (500 MHz, DMSO) δ 4.67 (2H, d, *J* = 3.7 Hz, H-2, 6), 4.20 (2H, dd, *J* = 8.6, 6.5 Hz, H-4, 8), 6.66 (4H, s, H-2''', 6''', 2', 6'), 4.88 (2H, d, *J* = 7.0 Hz, H-1'', 1''''), 3.76 (12H, s, H-3''', 5''', 3', 5'-OCH_3).

Syringaresinol-4'-O-glucopyranoside (**17**): $C_{28}H_{36}O_{13}$, amorphous solid; UV (MeOH) λ_{max} 229, 278 nm; ESI-MS *m/z*: 603.15 $[M+Na]^+$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 133.1 (C-1), 104.9 (C-2, 6), 149.4 (C-3, 5), 136.3 (C-4), 87.2 (C-7), 55.7 (C-8), 72.9 (C-9), 139.6 (C-1'), 104.6 (C-2', 6'),154.4 (C-3', 5'), 135.6 (C-4'), 87.6 (C-7'), 55.5 (C-8'), 72.9 (C-9'), 105.4 (C-1''), 75.7 (C-2''), 78.3 (C-3''), 77.8 (C-5''), 71.4 (C-4''), 62.6 (C-6''), 57.1 (C-3', 5'-OMe), 56.8 (C-3, 5-OMe). ^1H NMR (500 MHz, MeOH-d_4) δ 6.76 (2H, s, H-2, 6), 4.81 (1H, d, *J* = 4.1 Hz, H-7), 3.18 (2H, m, H-8, 8'), 6.70 (2H, s, H-2', 6'), 4.76 (1H, d, *J* = 4.3 Hz, H-7'), 4.32 (2H, m, H-9α, 9'α), 3.95 (2H, m, H-9β, 9'β), 4.90 (1H, d, *J* = 7.6, H-1''), 3.52 (1H, m, H-2''), 3.25 (1H, m, H-3''), 3.44 (1H, m, H-4''), 3.47 (1H, m, H-5''), 3.82 (1H, dd, *J* = 12.0, 2.4 Hz, H-6''α), 3.71 (1H, dd, *J* = 12.0, 5.2 Hz, H-6''β), 3.90 (6H, s, H-3, 5-OMe), 3.89 (6H, s, H-3', 5'-OMe).

Cycloolivil (**18**): $C_{20}H_{24}O_7$, yellow powder; $[\alpha]_D^{23.3}$ +47.61; UV (MeOH) λ_{max} 229, 285 nm; ESI-MS *m/z*: 421.68 $[M+HCOOH-H]^-$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 133.5 (C-1), 114.0 (C-2), 149.1 (C-3), 146.1 (C-4), 117.3 (C-5), 123.6 (C-6), 44.9 (C-7), 47.6 (C-8), 69.4 (C-9), 138.5 (C-1'), 113.0 (C-2'), 147.5 (C-3'), 145.3 (C-4'), 116.0 (C-5'), 126.4 (C-6'), 39.9 (C-7'), 75.0 (C-8'), 60.8 (C-9'), 56.4 (OCH_3), 56.4 (OCH_3). ^1H NMR (500 MHz, MeOH-d_4) δ 6.73 (1H, s, H-2), 6.79 (1H, d, *J* = 8.0 Hz, H-5), 6.69 (1H, dd, *J* = 7.9, 1.6 Hz, H-6), 4.05 (1H, d, *J* = 11.6 Hz, H-7), 2.05 (1H, m, H-8), 6.21 (1H, s, H-2'), 6.66 (1H, s, H-5'), 3.24 (1H, d, *J* = 16.6 Hz, H-7'a), 2.64 (1H, d, *J* = 16.7 Hz, H-7'b), 3.81 (2H, m, H-9a, 9'a), 3.60 (2H, m, H-9b, 9'b), 3.83(3H, s, OCH_3), 3.80 (3H, s, OCH_3).

Eucommiol (**19**): $C_9H_{16}O_4$, colorless syrup; $[\alpha]_D^{23.5}$ -30.84; UV (MeOH) λ_{max} 208 nm; ESI-MS *m/z*: 211.16 $[M+Na]^+$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 76.8 (C-1), 54.2 (C-2), 137.7 (C-3), 139.5 (C-4), 43.0 (C-5), 34.9 (C-2'), 57.0 (C-3'), 58.8 (C-4'), 61.8

(C-2''). ^{1}H NMR (500 MHz, MeOH-d_4) δ 4.12 (1H, s, H-1), 2.75 (1H, d, J = 9.5 Hz, H-2), 2.38 (1H, dd, J = 16.7, 2.9 Hz, H-5a), 2.82 (1H, dd, J = 16.7, 6.7 Hz, H-5b), 1.50 (1H, m, H-2'a), 1.95 (1H, m, H-2'b), 4.11 (1H, d, J = 12.7 Hz, H-3'a), 4.29 (1H, d, J = 12.7 Hz, H-3'b), 4.20 (2H, m, H-4'), 3.71 (2H, m, H-2'').

Eucommioside-I (**20**): $C_{15}H_{26}O_9$, colorless syrup; $[\alpha]_D^{23.1}$ -45.05; UV (MeOH) λ_{max} 207 nm; ESI-MS *m/z*: 373.31 $[M+Na]^+$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 76.4 (C-1), 54.2 (C-2), 137.7 (C-3), 139.6 (C-4), 43.1 (C-5), 32.1 (C-2'), 57.0 (C-3'), 58.8 (C-4'), 69.5 (C-2''), 104.5 (c-1'), 78.1 (c-3'), 78.0 (c-5'), 75.2 (c-2'), 71.6 (c-4'), 62.8 (c-6'). “c” in lowercase means glucoside. ^{1}H NMR (500 MHz, MeOH-d_4) δ 4.12 (2H, m, H-3'a, H-1), 2.84 (2H, m, H-2, 5b), 2.38 (1H, dd, *J* = 16.9, 2.1 Hz, H-5a), 1.52 (1H, m, H-2'a), 2.00 (1H, m, H-2'b), 4.29 (1H, d, *J* = 12.7 Hz, H-3'b), 4.20 (2H, m, H-4'), 3.73 (2H, m, H-2''), 4.32 (1H, d, *J* = 7.8 Hz, H-1').

Accubin (**21**): $C_{15}H_{22}O_9$, pale powder; UV (MeOH) λ_{max} 210 nm; ESI-MS *m/z*: 391.46 $[M+HCOOH-H]^-$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 97.7 (C-1), 141.5 (C-3), 105.7 (C-4), 46.2 (C-5), 82.8 (C-6), 130.3 (C-7), 148.0 (C-8), 47.9 (C-9), 61.4 (C-10), 99.9 (C-1'), 74.9 (C-2'), 78.2 (C-3'), 71.5 (C-4'), 77.9 (C-5'), 62.6 (C-6'). ^{1}H NMR (500 MHz, MeOH-d_4) δ 4.99 (1H, d, *J* = 7.1 Hz, H-1), 6.35 (1H, dd, *J* = 6.1, 1.9 Hz, H-3), 5.13 (1H, dd, *J* = 6.1, 3.9 Hz, H-4), 2.78 (1H, m, H-5), 4.47 (1H, m, H-6), 5.80 (1H, m, H-7), 3.01 (1H, m, H-9), 4.24 (2H, m, H-10α, β), 4.71 (1H, d, *J* = 7.0 Hz, H-1'), 3.23-3.47 (6H, m, H-2'-6').

Asperuliside (**22**): $C_{18}H_{22}O_{11}$, pale powder; UV (MeOH) λ_{max} 242 nm; ESI-MS *m/z*: 437.08 $[M+Na]^+$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 93.3 (C-1), 150.3 (C-3), 106.2 (C-4), 37.4 (C-5), 86.3 (C-6), 129.0 (C-7), 144.3 (C-8), 45.3 (C-9), 62.0 (C-10), 172.3 (C-11), 100.0 (C-1'), 74.6 (C-2'), 77.9 (C-3'), 71.6 (C-4'), 78.4 (C-5'), 62.8 (C-6'), 172.6 ($CH_3\underline{C}O$), 20.6 ($\underline{C}H_3CO$). ^{1}H NMR (500 MHz, MeOH-d_4) δ 6.00 (1H, d, *J* = 1.4 Hz, H-1), 7.35 (1H, d, *J* = 2.1 Hz, H-3), 3.72 (2H, m, H-5, 6'b), 5.61 (1H, dd, *J* = 5.0, 1.6 Hz, H-6), 5.78 (1H, m, H-7), 4.83 (1H, dd, *J* = 14.3, 1.3 Hz, H-10a), 4.71 (1H, dd, *J* = 14.3, 1.1 Hz, H-10b), 4.73 (1H, d, *J* = 7.9 Hz, H-1'), 3.97 (1H, dd, *J* = 11.9, 2.2 Hz , H-6'a), 3.20-3,47 (5H, m, H-2'-5', 9), 2.13 (3H, s, $C\underline{H_3}CO$).

Asperulosidic acid (**23**): $C_{18}H_{24}O_{12}$, amorphous solid; UV (MeOH) λ_{max} 207 nm; ESI-MS *m/z*: 455.02 $[M+Na]^+$; ^{13}C NMR (126 MHz, MeOH-d_4) δ 101.1 (C-1), 154.4 (C-

3), 109.6 (C-4), 42.8 (C-5), 75.6 (C-6), 131.8 (C-7), 146.0 (C-8), 46.4 (C-9), 63.8 (C-10), 172.5 (C-11), 100.6 (C-1'), 74.9 (C-2'), 78.5 (C-3'), 71.6 (C-4'), 77.9 (C-5'), 63.0 (C-6'), 172.5 (C-1"), 20.7 (C-2"). ^{1}H NMR (500 MHz, MeOH-d_4) δ 5.06 (1H, d, J = 9.0 Hz, H-1), 7.62 (1H, s, H-3), 3.06 (1H, t, J = 6.3 Hz, H-5), 3.27 (1H,m, H-6), 6.03 (1H, s, H-7), 2.64 (1H, m, H-9), 4.97 (1H, d, J = 15.1 Hz, H-10α), 4.83 (1H, d, J = 15.1 Hz, H-10β), 4.74 (1H, d, J = 7.8 Hz, H-1'), 2.11 (3H, s, H-2").

Blumenol C and 9-*epi*-Bluenol C (**24**): $C_{13}H_{22}O_2$, amorphous powder; UV (MeOH) λ_{max} 231 nm; ESI-MS *m/z*: 233.21 $[M+Na]^+$; ^{13}C signals could be devided into two groups according to their relative heights and they were assigned as follows:

Blumenol C (6R, 9R)

^{13}C NMR (126 MHz, MeOH-d_4) δ 37.3 (C-1), 48.0 (C-2), 202.2 (C-3), 125.4 (C-4), 169.7 (C-5), 52.4 (C-6), 27.3 (C-7), 39.8 (C-8), 68.6 (C-9), 23.7 (C-10), 29.0 (C-11), 27.4 (C-12), 24.8 (C-13).

9-*epi*-Bluenol C (6R, 9S)

^{13}C NMR (125 MHz, MeOH-d_4) δ 37.1 (C-1), 48.1 (C-2), 202.0 (C-3), 125.5 (C-4), 169.7 (C-5), 52.5 (C-6), 27.4 (C-7), 39.8 (C-8), 68.8 (C-9), 23.6 (C-10), 29.0 (C-11), 27.3 (C-12), 24.9 (C-13). ^{1}H NMR (500 MHz, MeOH-d_4) δ 2.48 (1H, d, J = 17.5 Hz, H-2a), 1.98 (1H, d, J = 17.5 Hz, H-2b), 5.84 (1H, s, H-4), 1.99 (1H, m, H-6), 1.80 (1H, m, H-7a), 1.76 (1H, m, H-7b), 1.56 (2H, m, H-8a, 8b), 3.71 (1H, m, H-9), 1.20 (3H, d, J = 6.2 Hz, H-10), 1.05 (3H, s, H-11), 1.12 (3H, s, H-12), 2.07 (3H, s, H-13).

Foliasalacioside B_1 (**25**): $C_{24}H_{40}O_{11}$, amorphous powder; $[\alpha]_D^{22.6}$ +52.17; UV (MeOH) λ_{max} 235 nm; ESI-MS *m/z*: 503.53 $[M-H]^-$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 37.3 (C-1), 48.1 (C-2), 202.4 (C-3), 125.4 (C-4), 170.2 (C-5), 52.5 (C-6), 26.9 (C-7), 37.9 (C-8), 75.7 (C-9), 20.1 (C-10), 27.6 (C-11), 29.1 (C-12), 25.0 (C-13), 102.3 (C-1'), 75.1 (C-2'), 78.1 (C-3'), 71.8 (C-4'), 76.8 (C-5'), 69.3 (C-6'), 105.2 (C-1"), 72.4 (C-2"), 74.2 (C-3"), 69.8 (C-4"), 66.5 (C-5"). ^{1}H NMR (500 MHz, MeOH-d_4) δ 2.50 (1H, d, J = 17.4 Hz, H-2a), 2.00 (1H, d, J = 17.6 Hz, H-2b), 5.84 (1H, s, H-4), 2.01 (1H, m, H-6), 1.52 (1H, m, H-7a), 1.68 (3H, m, H-7b, 8a, 8b), 3.88 (1H, m, H-9), 1.21 (3H, d, J = 6.1 Hz, H-10), 1.13 (3H, s, H-11), 1.04 (3H, s, H-12), 2.09 (3H, s, H-13), 4.35 (1H, d, J = 7.7 Hz, H-1'), 4.32 (1H, d, J = 6.7 Hz, H-1").

Foliasalacioside E_2 (**26**): $C_{24}H_{42}O_{11}$, amorphous solid; UV (MeOH) λ_{max} 206 nm; ESI-MS *m/z*: 505.29 $[M-H]^-$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 38.8 (C-1), 49.5 (C-2), 65.7 (C-3), 42.9 (C-4), 125.4 (C-5), 138.4 (C-6), 25.4 (C-7), 39.0 (C-8), 76.3 (C-9), 19.8 (C-10), 29.0 (C-11), 30.4 (C-12), 20.1 (C-13), 102.2 (C-1'), 75.1 (C-2'), 78.1 (C-3'), 71.8 (C-4'), 76.9 (C-5'), 69.7 (C-6'), 105.2 (C-1''), 72.4 (C-2''), 74.2 (C-3''), 69.4 (C-4''), 66.6 (C-5''); ^1H NMR (500 MHz, MeOH-d_4) δ 1.72 (1H, m, H-2a), 1.41 (1H, dd, *J* = 11.6, 11.6 Hz, H-2b), 3.87 (1H, m, H-3), 2.20 (1H, m, H-4a), 1.95 (1H, m, H-4b), 2.24 (1H, m, H-7a), 2.03 (1H, m, H-7b), 1.59 (2H, m, H-8a, 8b), 3.91 (1H, m, H-9), 1.23 (3H, d, *J* = 6.1 Hz, H-10), 1.07 (3H, s, H-11), 1.09 (3H, s, H-12), 1.68 (3H, s, H-13), 4.37 (1H, d, *J* = 7.7 Hz, H-1'), 4.38 (1H, d, *J* = 6.6 Hz, H-1'').

Icariside F_2 (**27**): $C_{18}H_{26}O_{10}$, amorphous powder; UV (MeOH) λ_{max} 211 nm; ESI-MS *m/z*: 425.33 $[M+Na]^+$; ^{13}C NMR (125 MHz, MeOH-d_4) δ 139.0 (C-1), 129.3 (C-2), 129.3 (C-3), 128.7 (C-4), 129.3 (C-5), 129.3 (C-6), 71.8 (C-7), 103.2 (C-1'), 75.1 (C-2'), 78.0 (C-3'), 71.8 (C-4'), 77.0 (C-5'), 68.7 (C-6'), 111.0 (C-1''), 78.0 (C-2''), 80.5 (C-3''), 75.0 (C-4''), 65.6 (C-5''); ^1H NMR (500 MHz, MeOH-d_4) δ 7.28 – 7.70 (5H, m, H-2, 3, 4, 5, 6), 4.69 (1H, d, *J* = 11.8 Hz, H-7a), 4.93 (1H, d, *J* = 11.8 Hz, H-7b), 4.37 (1H, d, *J* = 7.7 Hz, H-1'), 5.09 (1H, d, *J* = 2.5 Hz, H-1'').