Supplementary information

Isolation and Characterization of Auronlignan Derivatives with Hepatoprotective and Hypolipidemic Activities from the Fruits of *Hippophae rhamnoides* L.¹

Qinge Ma,^a Yang Guan,^a Jianghong Dong,^d Zhipei Sang,^{b,c,*} Rongrui Wei^{a,*}

^aKey Laboratory of Modern Preparation of Traditional Chinese Medicine of Ministry of Education, Research Center of Natural Resources of Chinese Medicinal Materials and Ethnic Medicine, Science and Technology College, Jiangxi University of Traditional Chinese Medicine, Nanchang 330004 China ^bCollege of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, China ^cSchool of Pharmaceutical Sciences, Hanan University, Haikou 570228, China ^dCollege of Chemistry and Pharmaceutical Engineering, Huanghuai University, Zhumadian 463000, China

¹*Corresponding authors.

E-mail: weirongrui2011@163.com (R.-R Wei); sangzhipei@126.com (Z.-P Sang).

Contents

1. Table S1 ¹ H	I NMR (400 MHz, Acetone- d_6) and ¹³ C NMR (100 M	Hz, Acetone- d_6)
of	compounds	(1-
3)		.3
2. Table S2 ¹ H	I NMR (400 MHz, Acetone- d_6) and ¹³ C NMR (100 M	Hz, Acetone- <i>d</i> ₆)
of	compounds	(4-
6)		.4
 6) 3. Table S3 ¹H 	I NMR (400 MHz, Acetone- d_6) and ¹³ C NMR (100 M	4 Hz, Acetone-d ₆)
 6) 3. Table S3 ¹H of 	I NMR (400 MHz, Acetone- <i>d</i> ₆) and ¹³ C NMR (100 M compounds	4 Hz, Acetone- <i>d</i> ₆) (7-
 6) 3. Table S3 ¹H of 9) 	I NMR (400 MHz, Acetone- <i>d</i> ₆) and ¹³ C NMR (100 M compounds	4 Hz, Acetone- <i>d</i> ₆) (7- 5

No.	1		2		3	
	$\delta_{ m H}$	$\delta_{ m C}$	$\delta_{ m H}$	δ_{C}	$\delta_{ m H}$	$\delta_{\rm C}$
1	-	-	-	-	-	-
2	-	143.6	-	143.7	-	143.6
3	-	182.1	-	182.1	-	182.1
4	7.83(dd.2.0.8.0)	127.8	7.84(dd.2.0.8.0)	127.9	7.83(dd.2.0.8.0)	127.8
5	6.41(d.8.0)	114.7	6.41(d.8.0)	114.7	6.41(d.8.0)	114.7
6	-	164.7	-	164.7	-	164.7
7	6.44(d.2.0)	101.9	6.45(d.2.0)	101.8	6.44(d.2.0)	101.9
8	-	168.2	-	168.4	-	168.2
9	-	116.2	-	116.3	-	116.2
10	-	128.3	-	128.3	-	128.3
1'	-	130.8	-	129.7	-	130.9
2'	6.91(s)	107.1	6.11(s)	111.4	6.12(s)	111.8
3'	-	151.2	-	150.7	-	151.1
4'	-	142.4	-	134.1	-	132.4
5'	-	127.0	-	147.0	-	151.1
6'	7.30(s)	112.4	6.23(s)	106.5	6.12(s)	111.8
1"	-	-	-	-	-	-
2"	-	143.6	-	143.7	-	143.6
3"	-	182.1	-	182.1	-	182.1
4"	7.83(dd.2.0.8.0)	127.8	7.84(dd.2.0.8.0)	127.9	7.83(dd.2.0.8.0)	127.8
5"	6.41(d.8.0)	114.7	6.41(d.8.0)	114.7	6.41(d.8.0)	114.7
6"	-	164.7	-	164.7	-	164.7
7"	6.44(d.2.0)	101.9	6.45(d.2.0)	101.8	6.44(d.2.0)	101.9
8"	-	168.2	-	168.4	-	168.2
9"	-	116.2	-	116.3	-	116.2
10"	-	128.1	-	128.1	-	128.1
1'''	-	126.2	-	126.3	-	126.2
2'''	7.31(d.8.0)	128.5	7.33(d.8.0)	129.4	7.32(d.8.0)	128.8
3'''	6.62(d.8.0)	116.6	6.63(d.8.0)	116.7	6.62(d.8.0)	116.7
4'''	-	156.4	-	157.0	-	156.4
5'''	6.62(d.8.0)	116.6	6.63(d,8.0)	116.7	6.62(d,8.0)	116.7
6'''	7.31(d.8.0)	128.5	7.33(d,8.0)	129.4	7.32(d,8.0)	128.8
1''''	-	125.2	-	124.5	-	134.2
2""	7.45(d.8.0)	126.4	7.13(dd,2.0,8.0)	121.4	6.37(s)	105.0
3''''	6.83(d.8.0)	117.2	6.92(d.8.0)	117.6	-	148.8
4""	-	157.8	-	148.0	-	137.1
5""	6.83(d.8.0)	117.2	-	150.6	-	148.8
6''''	7.45(d.8.0)	126.4	6.65(d.2.0)	112.1	6.37(s)	105.0
7''''	-	152.0	-	126.2	7.01(s)	129.2
8''''	-	114.1	-	124.8	-	122.2
9""	4.63(s)	51.2	4.21(s)	48.6	4.22(s)	57.2
3""-OCH3	-	-	-	-	3.84(s)	56.2
5""-OCH ₃	-	-	3.85(s)	56.4	3.84(s)	56.2

Table S1 ¹H NMR (400 MHz, Acetone- d_6) and ¹³C NMR (100 MHz, Acetone- d_6) of compounds (1-3).

No.	4		5		6	
	$\delta_{ m H}$	$\delta_{ m C}$	$\delta_{ m H}$	$\delta_{ m C}$	$\delta_{ m H}$	$\delta_{ m C}$
1	-	-	-	-	-	-
2	-	143.3	-	143.2	-	143.1
3	-	182.3	-	182.3	-	182.3
4	7.83(d,8.0)	125.0	8.28(d,8.0)	130.3	7.89(d,8.0)	126.4
5	7.02(d,8.0)	110.2	6.82(d,8.0)	112.9	7.04(d,8.0)	111.3
6	-	164.8	-	162.9	-	163.5
7	-	113.1	-	113.4	-	111.9
8	-	157.9	-	158.5	-	159.1
9	-	115.0	-	114.9	-	115.2
10	-	124.1	-	124.1	-	124.1
11	3.49(d,7.0)	22.5	-	197.2	3.65(s)	40.3
12	5.42(t,7.0,1.5)	122.6	2.72(s)	49.2	-	210.8
13	-	132.9	-	88.6	2.72(m)	40.5
1'	-	131.3	-	134.8	-	136.1
2'	6.95(s)	107.4	6.09(s)	109.0	6.10(s)	106.2
3'	-	151.0	-	150.9	-	150.6
4'	-	142.2	-	133.7	-	131.7
5'	-	127.3	-	146.8	-	150.6
6'	7.36(s)	111.9	6.13(s)	107.6	6.10(s)	106.2
1"	-	128.2	-	128.2	-	-
2"	6.95(d,8.0)	130.8	6.96(d,8.0)	130.9	6.95(d,8.0)	130.8
3"	6.63(d,8.0)	116.3	6.62(d.8.0)	116.5	6.62(d,8.0)	116.5
4"	-	156.1	-	156.2	-	156.1
5"	6.63(d,8.0)	116.3	6.62(d,8.0)	116.5	6.62(d,8.0)	116.5
6"	6.95(d,8.0)	130.8	6.96(d,8.0)	130.9	6.95(d,8.0)	130.8
7"	3.24(s)	42.3	3.24(s)	42.3	3.24(s)	42.3
1'''	-	125.2	-	124.5	-	134.2
2'''	7.45(d,8.0)	126.4	7.13(dd,2.0,8.0)	121.4	6.37(s)	105.0
3'''	6.83(d,8.0)	117.2	6.92(d,8.0)	117.6	-	148.8
4'''	-	157.8	-	148.0	-	137.1
5'''	6.83(d.8.0)	117.2	-	150.6	-	148.8
6'''	7.45(d.8.0)	126.4	6.65(d,2.0)	112.1	6.37(s)	105.0
7'''	-	152.0	-	126.2	7.01(s)	129.2
8'''	-	114.1	-	124.8	-	122.2
9'''	4.63(s)	51.2	4.21(s)	48.6	4.22(s)	57.2
14-CH ₃	1.69(s)	25.9	1.41(s)	27.4	1.18(d,6.9)	17.8
15-CH ₃	1.88(s)	18.3	1.41(s)	27.4	1.18(d,6.9)	17.8
3""-OCH ₃	-	-	-	-	3.84(s)	56.2
5'''-OCH ₃	-	-	3.85(s)	56.4	3.84(s)	56.2

Table S2 ¹H NMR (400 MHz, Acetone- d_6) and ¹³C NMR (100 MHz, Acetone- d_6) of compounds (4-6).

No.	7		8		9	
	$\delta_{ m H}$	$\delta_{ m C}$	$\delta_{ m H}$	$\delta_{ m C}$	$\delta_{ m H}$	$\delta_{ m C}$
1	-	-	-	-	-	-
2	-	143.1	-	143.2	-	143.1
3	-	179.8	-	179.8	-	179.8
4	7.84(d,8.0)	125.2	7.80(d,8.0)	126.8	7.76(d,8.0)	127.0
5	7.03(d,8.0)	110.4	6.62(d,8.0)	113.6	6.55(d,8.0)	112.2
6	-	164.7	-	158.9	-	162.6
7	-	113.2	-	110.7	-	114.7
8	-	158.2	-	157.4	-	157.1
9	-	115.1	-	114.7	-	115.0
10	-	142.9	-	142.8	-	142.7
11	3.50(d,7.0)	22.7	6.67(d,10.0)	115.9	6.89(d,16.5)	121.6
12	5.42(t,7.0,1.5)	122.6	5.75(d,10.0)	128.5	6.70(d,16.5)	116.9
13	-	132.9	-	81.8	-	81.5
1'	-	131.5	-	128.8	-	127.6
2'	6.93(s)	107.6	6.11(s)	109.4	6.12(s)	107.0
3'	-	151.1	-	149.9	-	149.9
4'	-	142.4	-	133.9	-	131.9
5'	-	127.4	-	146.5	-	149.9
6'	7.34(s)	111.7	6.16(s)	107.5	6.12(s)	107.0
1"	5.51(d,7.8)	101.8	5.50(d,7.8)	101.6	5.51(d,7.8)	101.7
2"	3.76(m)	75.1	3.74(m)	75.0	3.75(m)	75.1
3"	3.88(m)	78.6	3.86(m)	78.4	3.86(m)	78.5
4"	3.41(m)	72.1	3.40(m)	72.0	3.41(m)	72.2
5"	3.79(m)	74.6	3.79(m)	74.5	3.79(m)	74.4
6"a	3.49(dd,11.2,6.4)	62.7	3.50(dd,11.2,6.4)	62.6	3.51(dd,11.2,6.4)	62.6
6''b	3.90(dd,11.2,3.2)	62.7	3.92(dd,11.2,3.2)	62.6	3.93(dd,11.2,3.2)	62.6
1'''	-	125.3	-	124.3	-	134.1
2""	7.46(d,8.0)	126.5	7.14(dd,2.0,8.0)	121.6	6.37(s)	105.2
3'''	6.84(d,8.0)	117.1	6.93(d,8.0)	117.6	-	148.6
4'''	-	157.9	-	148.2	-	137.0
5'''	6.84(d.8.0)	117.1	-	150.8	-	148.6
6'''	7.46(d.8.0)	126.5	6.65(d,2.0)	112.2	6.37(s)	105.2
7'''	-	152.0	-	126.4	7.01(s)	130.0
8'''	-	114.1	-	124.7	-	122.1
9'''	4.63(s)	51.3	4.20(s)	48.7	4.22(s)	57.2
14-CH ₃	1.70(s)	26.0	1.45(s)	28.1	1.46(s)	28.4
15-CH ₃	1.88(s)	18.4	1.45(s)	28.1	1.46(s)	28.4
3'''-OCH ₃	-	-	-	-	3.84(s)	56.2
5""-OCH ₃	-	-	3.85(s)	56.5	3.84(s)	56.2

Table S3 ¹H NMR (400 MHz, Acetone- d_6) and ¹³C NMR (100 MHz, Acetone- d_6) of compounds (7-9).

4. Data information of compounds (1-9).

3,3',4''',6,6''-tetrahydroxy-7'''',8''''-(4''''-hydroxy-1''''-cinnamylalcohol)-10,10''biauronlignan (1): a yellow amorphous powder, HR-ESI-MS: m/z 669.1395 [M + H]⁺ (calc. for C₃₉H₂₅O₁₁, 669.1397); UV (MeOH) λ_{max} : 204, 255, 335, 402 nm; IR (KBr) v_{max} : 3452, 1668, 1605, 1514, 1385 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S1.

3',4''',6,6"-tetrahydroxy-7'''',8''''-(4''''-hydroxy-5''''-methoxy-1''''-cinnamylalcohol)-10,10"-biauronlignan (**2**): a yellow amorphous powder, HR-ESI-MS: m/z 715.1453 $[M + H]^+$ (calc. for C₄₀H₂₇O₁₃, 715.1452); UV (MeOH) λ_{max} : 205, 255, 335, 401 nm; IR (KBr) v_{max} : 3454, 1668, 1606, 1513, 1387 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S1.

3',4''',6,6''-tetrahydroxy-4'-(4''''-hydroxy-3'''',5''''-dimethoxy-1''''-cinnamylalcohol)-10,10''-biauronlignan (**3**): a yellow amorphous powder, HR-ESI-MS: m/z 747.1716 $[M + H]^+$ (calc. for C₄₁H₃₀O₁₄, 747.1714); UV (MeOH) λ_{max} : 207, 255, 335, 403 nm; IR (KBr) v_{max} : 3453, 1668, 1606, 1511, 1386 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S1.

3',6-dihydroxy-7-prenyl-7"',8"'-(4"'-hydroxy-1"'-cinnamylalcohol)-10-(4"-

hydroxy-benzyl)-auronlignan (4): a yellow amorphous powder, HR-ESI-MS: m/z591.2017 [M + H]⁺ (calc. for C₃₆H₃₁O₈, 591.2019); UV (MeOH) λ_{max} : 203, 256, 275, 403 nm; IR (KBr) v_{max} : 3348, 1674, 1608, 1507, 1387 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S2.

3'-hydroxy-6,7-(14,15-dimethyl-11-cyclohexanone)-7"",8"'-(4"'-hydroxy-5""-

methoxy-1"'-cinnamylalcohol)-10-(4"-hydroxy-benzyl)-auronlignan (5): a yellow amorphous powder, HR-ESI-MS: m/z 651.1863 [M + H]⁺ (calc. for C₃₇H₃₁O₁₁, 651.1866); UV (MeOH) λ_{max} : 202, 255, 275, 404 nm; IR (KBr) v_{max} : 3346, 1674, 1607, 1508, 1388 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S2.

3'/5'/6-trihydroxy-7-(14,15-dimethylbutan-12-one)-4'-(4'''-hydroxy-3''',5'''methoxy-1'''-cinnamylalcohol)-10-(4''-hydroxy-benzyl)-auronlignan (6): a yellow amorphous powder, HR-ESI-MS: m/z 685.2282 [M + H]⁺ (calc. for C₃₈H₃₇O₁₂, 685.2285); UV (MeOH) λ_{max} : 204, 254, 275, 401 nm; IR (KBr) v_{max} : 3343, 1676, 1604, 1509, 1387 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S2.

3',6-dihydroxy-7-prenyl-7''',8'''-(4'''-hydroxy-1'''-cinnamylalcohol)-10-O- β -Dglucopyranosyl-auronlignan (7): a yellow amorphous powder, HR-ESI-MS: *m/z* 663.2079 [M + H]⁺ (calc. for C₃₅H₃₅O₁₃, 663.2078); UV (MeOH) λ_{max} : 203, 255, 275, 402 nm; IR (KBr) v_{max} : 3346, 1675, 1610, 1511, 1388 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S3.

3'-hydroxy-6,7-(14,15-dimethylchromeneprenyl)-7"",8"'-(4"'-hydroxy-5""-

methoxy-1"'-cinnamylalcohol)-10-O-β-D-glucopyranosyl-auronlignan (8): a yellow amorphous powder, HR-ESI-MS: m/z 707.1973 [M + H]⁺ (calc. for C₃₆H₃₅O₁₅, 707.1976); UV (MeOH) λ_{max} : 202, 255, 275, 403 nm; IR (KBr) v_{max} : 3348, 1674, 1608, 1506, 1389 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S3.

3',5',6-trihydroxy-7-isopentenol-7''',8'''-(4'''-hydroxy-3''',5'''-methoxy-1'''-cinnamyl alcohol)-10-O-β-D-glucopyranosyl-auronlignan (9): a yellow amorphous powder, HR-ESI-MS: m/z 757.2348 [M + H]⁺ (calc. for C₃₇H₄₁O₁₇, 757.2344); UV (MeOH) λ_{max} : 205, 254, 275, 402 nm; IR (KBr) v_{max} : 3345, 1677, 1607, 1510, 1386 cm⁻¹; ¹H NMR and ¹³C NMR data were shown in Table S3.