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Article

New Rare Sinapoyl Acylated Flavonoid Glycosides Obtained from the Seeds of *Lepidium apetalum* Willd

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Abstract: Seven new rare sinapoyl acylated flavonoid glycosides, apetalumosides A_1 (**1**), B_8 (**2**), B_9 (**3**), B_{10} (**4**), B_{11} (**5**), B_{12} (**6**), and C_1 (**7**) were isolated from the seeds of *Lepidium apetalum* Willd. Their structures were elucidated by chemical and spectroscopic methods.

Keywords: *Lepidium apetalum*; seeds; sinapoyl acylated flavonoid glycosides

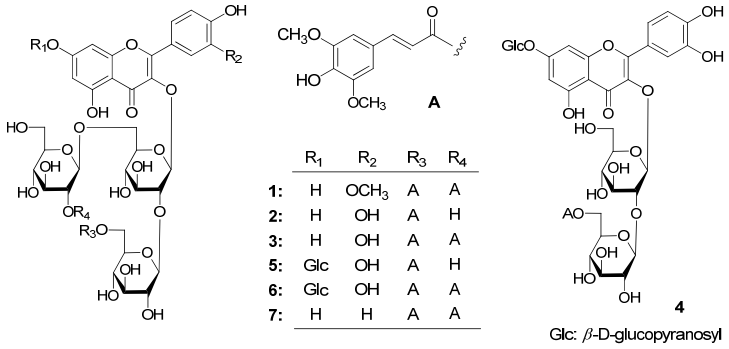
1. Introduction

In the course of our characterization studies on bioactive constituents from *Lepidium apetalum* Willd [1], we have reported the isolation and structure elucidation of nine new flavonoid glycosides, apetalumosides A, B_1–B_7, and C, together with one known isolate, quercetin 3-*O*-(2,6-di-*O*-β-D-glucopyranosyl)-β-D-glucopyranoside obtained from the seeds of it. As a continuing study on *L. apetalum* seeds, we have isolated seven new rare sinapoyl acylated flavonoid glycosides, named as apetalumosides

A_1 (**1**), B_8 (**2**), B_9 (**3**), B_{10} (**4**), B_{11} (**5**), B_{12} (**6**), and C_1 (**7**) from the herbal medicine. In this paper, we describe the isolation and structure elucidation of these new ones.

2. Results and Discussion

The seeds of *L. apetalum* were refluxed with 50% ethanol/water. Evaporation of the solvent under reduced pressure provided a 50% ethanol/water extract. The extract was subjected to kinds of column chromatography (CC) and finally preparative HPLC (PHPLC) to yield seven new rare sinapoyl acylated flavonoid glycosides, apetalumosides A_1 (**1**), B_8 (**2**), B_9 (**3**), B_{10} (**4**), B_{11} (**5**), B_{12} (**6**), and C_1 (**7**) (Figure 1).



	R_1	R_2	R_3	R_4
1:	H	OCH_3	A	A
2:	H	OH	A	H
3:	H	OH	A	A
5:	Glc	OH	A	H
6:	Glc	OH	A	A
7:	H	H	A	A

Figure 1. The structure of compounds **1**–**7**. (**A**), the moiety structure which indicated in the table for compounds **1**–**3** and **5**–**7**; (**4**), an isolated structure of B_{10} (**4**).

Apetalumoside A1 (**1**), $[\alpha]_D^{25}$ –49.0° (MeOH), was isolated as yellow powder. The IR spectrum of **1** showed absorption bands ascribable to hydroxyl (3394 cm^{-1}), α,β-unsaturated ester (1701, 1630 cm^{-1}), aromatic ring (1648, 1604, 1514, 1458 cm^{-1}), and *O*-glycosidic linkage (1075 cm^{-1}). The molecular formula, $C_{56}H_{62}O_{30}$, of **1** was eatablished by negative-ion HRESI-TOF-MS (*m*/*z* 1213.3238 $[M - H]^-$, calcd for $C_{56}H_{61}O_{30}$ 1213.3253). Acid hydrolysis of it yielded D-glucose, which was identified by retention time and optical rotation using chiral detection by HPLC analysis [1,2]. The ^1H and ^{13}C-NMR (DMSO-d_6, Table 1) spectra of **1** showed signals assignable to an isorhamnetin aglycon [δ 3.85 (3H, s, 3′-OCH_3), 6.18 (1H, br. s, H-6), 6.32 (1H, br. s, H-8), 6.90 (1H, d, *J* = 8.5 Hz, H-5′), 7.60 (1H, dd, *J* = 1.5, 8.5 Hz, H-6′), 7.74 (1H, d, *J* = 1.5 Hz, H-2′), 12.74 (1H, br. s, 5-OH)], three β-D-glucopyranosyl groups [δ 4.33 (1H, d, *J* = 8.0 Hz, H-1‴′), 4.67 (1H, d, *J* = 7.5 Hz, H-1‴), 5.74 (1H, d, *J* = 7.0 Hz, H-1″)], together with two sinapoyl {6‴-sinapoyl: δ_H 3.77 (6H, s, 3‴″,5‴″-OCH_3), 6.27 (1H, d, *J* = 15.5 Hz, H-8‴″), 6.81 (2H, s, H-2‴″,6‴″), 7.38 (1H, d, *J* = 15.5 Hz, H-7‴″), and δ_C 166.4 (C-9‴″); 2‴′-sinapoyl: δ_H 3.91 (6H, s, 3‴‴″,5‴‴″-OCH_3), 6.28 (1H, d, *J* = 16.0 Hz, H-8‴‴″), 7.08 (2H, s, H-2‴‴″,6‴‴″), 7.51 (1H, d, *J* = 16.0 Hz, H-7‴‴″), and δ_C 165.6 (C-9‴‴″)]. The ^1H ^1H COSY experiment (Figure 2) on **1** indicated the presence of partial structure written in bold lines. To assign the badly overlapped protons in sugar chemical shift range, HSQC-TOCSY experiment was determined. In the HSQC-TOCSY spectrum, the correlations between the following proton and carbon pairs were observed: δ_C 98.2 (C-1″) and δ_H 3.04 (H-4″), 3.21 (H-5″), 3.46 (H-3″), 3.51 (H-2″), 5.74 (H-1″); δ_C 66.7 (C-6″) and δ_H 3.04 (H-4″), 3.21 (H-5″), 3.50, 3.75 (H_2-6″); δ_C 103.8 (C-1‴) and δ_H 3.15 (H-2‴), 3.24 (H-4‴), 3.25 (H-3‴), 3.40 (H-5‴), 4.67 (H-1‴); δ_C 63.3 (C-6‴) and δ_H 3.24 (H-4‴), 3.40 (H-5‴), 4.20, 4.27 (H_2-6‴); δ_C 100.2 (C-1‴′) and δ_H 2.68 (H-5‴′), 2.87 (H-3‴′), 3.15 (H-4‴′), 4.33 (H-1‴′), 4.45 (H-2‴′); δ_C 60.3 (C-6‴′)

and δ_H 2.68 (H-5‴), 2.87 (H-3‴), 3.15 (H-4‴), 3.41, 3.48 (H_2-6‴). Finally, in the HMBC experiment (Figure 2), long-range correlations were observed between δ_H 5.74 (H-1″) and δ_C 132.7 (C-3); δ_H 4.67 (H-1‴) and δ_C 82.1 (C-2″); δ_H 4.33 (H-1⁗) and δ_C 66.7 (C-6″); δ_H 4.20, 4.27 (H_2-6‴) and δ_C 166.4 (C-9⁗); δ_H 4.45 (H-2⁗) and δ_C 165.6 (C-9⁗), then the connectivities between oligoglycoside moieties and aglycon or sinapoyl groups were characterized. On the basis of above mentioned evidence, the structure of apetalumoside A_1 (**1**) was elucidated to be isorhamnetin 3-*O*-[β-D-(2-*O*-sinapoyl)-glucopyranosyl(1→6)]-β-D-(6-*O*-sinapoyl)-glucopyranosyl(1→2)-β-D-glucopyranoside.

Table 1. ^{1}H and ^{13}C-NMR data for **1** in DMSO-d_6 (500 MHz for ^{1}H and 125 MHz for ^{13}C).

No.	δ_C	δ_H (*J* in Hz)	No.	δ_C	δ_H (*J* in Hz)
2	155.9	-	4‴	69.6	3.24 (dd, 9.0, 9.0)
3	132.7	-	5‴	73.9	3.40 (m)
4	177.3	-	6‴	63.3	4.20 (br. d, *ca.* 12)
5	161.1	-			4.27 (dd, 5.5, 12.0)
6	98.9	6.18 (br. s)	1⁗	100.2	4.33 (d, 8.0)
7	164.7	-	2⁗	73.6	4.45 (dd, 8.0, 9.0)
8	94.0	6.32 (br. s)	3⁗	74.2	2.87 (dd, 9.0, 9.0)
9	156.2	-	4⁗	69.9	3.15 (dd, 8.0, 9.0)
10	103.8	-	5⁗	76.4	2.68 (m)
1′	120.9	-	6⁗	60.3	3.41 (dd, 5.0, 11.0)
2′	112.7	7.74 (d, 1.5)			3.48 (br. d, *ca.* 11)
3′	147.0	-	1⁗	124.2	-
4′	149.6	-	2⁗,6⁗	106.0	6.81 (s)
5′	115.3	6.90 (d, 8.5)	3⁗,5⁗	147.9	-
6′	122.8	7.60 (dd, 1.5, 8.5)	4⁗	138.2	-
5-OH	-	12.74 (br. s)	7⁗	145.2	7.38 (d, 15.5)
3′-OCH_3	55.7	3.85 (s)	8⁗	114.3	6.27 (d, 15.5)
1″	98.2	5.74 (d, 7.0)	9⁗	166.4	-
2″	82.1	3.51 (dd, 7.0, 8.5)	3⁗,5⁗-OCH_3	55.9	3.77 (s)
3″	76.3	3.46 (dd, 8.5, 8.5)	1⁗	124.6	-
4″	69.4	3.04 (dd, 8.5, 9.0)	2⁗,6⁗	106.0	7.08 (s)
5″	78.1	3.21 (m)	3⁗,5⁗	148.1	-
6″	66.7	3.50 (dd, 4.5, 11.5)	4⁗	138.3	-
		3.75 (br. d, *ca.* 12)	7⁗	145.3	7.51 (d, 16.0)
1‴	103.8	4.67 (d, 7.5)	8⁗	114.8	6.28 (d, 16.0)
2‴	74.3	3.15 (dd, 7.5, 8.0)	9⁗	165.6	-
3‴	76.3	3.25 (dd, 8.0, 9.0)	3⁗,5⁗-OCH_3	56.2	3.91 (s)

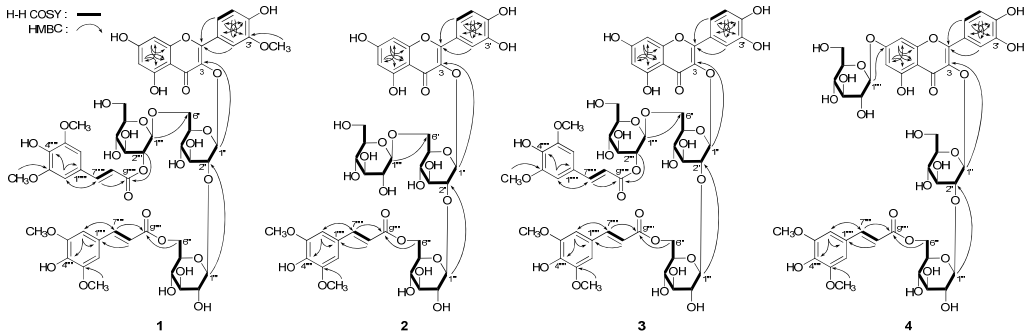


Figure 2. The main ^{1}H ^{1}H COSY and HMBC correlations of **1**–**4**.

Apetalumoside B8 (**2**), was obtained as yellow powder with negative rotation ($[\alpha]_D^{25}$ –41.6°, in MeOH). The molecular formula, $C_{44}H_{50}O_{26}$, of **2** was determined by negative-ion HRESI-TOF-MS (*m*/*z* 993.2522 $[M - H]^-$, calcd for $C_{44}H_{49}O_{26}$ 993.2518). Acid hydrolysis of it yielded D-glucose, which was identified by the same method as **1** [1,2]. The ^1H and ^{13}C (DMSO-d_6, Table 2) and various 2D NMR experiments including ^1H ^1H COSY, HSQC, HMBC, and HSQC-TOCSY spectra of **2** indicated the presences of a quercetin aglycon [δ 6.16 (1H, d, *J* = 2.0 Hz, H-6), 6.26 (1H, d, *J* = 2.0 Hz, H-8), 6.89 (1H, d, *J* = 8.5 Hz, H-5′), 7.55 (1H, d, *J* = 2.0 Hz, H-2′), 7.59 (1H, dd, *J* = 2.0, 8.5 Hz, H-6′), 12.64 (1H, br. s, 5-OH)], three β-D-glucopyranosyls [δ 4.03 (1H, d, *J* = 7.5 Hz, H-1‴′), 4.69 (1H, d, *J* = 7.5 Hz, H-1‴), 5.65 (1H, d, *J* = 7.0 Hz, H-1″)], and a sinapoyl [δ_H 3.77 (6H, s, 3⁗,5⁗-OCH_3), 6.30 (1H, d, *J* = 16.0 Hz, H-8⁗), 6.83 (2H, s, H-2⁗,6⁗), 7.39 (1H, d, *J* = 16.0 Hz, H-7⁗); δ_C 166.4 (C-9⁗)]. According to the correlations from ^1H ^1H COSY, HSQC, and HSQC-TOCSY experiments, the ^1H and ^{13}C-NMR data for three β-D-glucopyranosyl groups were assigned in detail. Furthermore, in the HMBC experiments, long-range correlations between δ_H 5.65 (H-1″) and δ_C 132.8 (C-3); δ_H 4.69 (H-1‴) and δ_C 83.0 (C-2″); δ_H 4.03 (H-1‴′) and δ_C 67.8 (C-6″); δ_H 4.21, 4.31 (H_2-6‴) and δ_C 166.4 (C-9⁗) were observed (Figure 2). Consequently, the structure of apetalumoside B_8 (**2**) was determined as quercetin 3-*O*-[β-D-glucopyranosyl(1→6)]-β-D-(6-*O*-sinapoyl)-glucopyranosyl(1→2)-β-D-glucopyranoside.

Table 2. ^1H and ^{13}C-NMR data for **2** in DMSO-d_6 (500 MHz for ^1H and 125 MHz for ^{13}C).

No.	δ_C	δ_H (*J* in Hz)	No.	δ_C	δ_H (*J* in Hz)
2	155.5	-	1‴	104.3	4.69 (d, 7.5)
3	132.8	-	2‴	74.3	3.17 (dd, 7.5, 8.5)
4	177.2	-	3‴	76.2	3.26 (dd, 8.5, 9.0)
5	161.1	-	4‴	69.4	3.29 (dd, 9.0, 9.0)
6	98.6	6.16 (d, 2.0)	5‴	73.8	3.51 (m)
7	164.1	-	6‴	63.0	4.21 (br. d, *ca.* 11)
8	93.4	6.26 (d, 2.0)			4.31 (dd, 5.0, 11.0)
9	156.1	-	1⁗	103.2	4.03 (d, 7.5)
10	103.7	-	2⁗	73.2	2.83 (dd, 7.5, 8.5)
1′	121.0	-	3⁗	76.4	2.96 (dd, 8.5, 8.5)
2′	116.1	7.55 (d, 2.0)	4⁗	69.6	3.02 (dd, 8.5, 8.5)
3′	144.8	-	5⁗	76.4	2.87 (m)
4′	148.4	-	6⁗	60.7	3.40 (dd, 5.0, 11.5)
5′	115.2	6.89 (d, 8.5)			3.55 (br. d, *ca.* 12)
6′	121.8	7.59 (dd, 2.0, 8.5)	1⁗′	124.2	-
5-OH	-	12.64 (br. s)	2⁗,6⁗′	105.8	6.83 (s)
1″	98.0	5.65 (d, 7.0)	3⁗′,5⁗′	147.8	-
2″	83.0	3.53 (dd, 7.0, 8.5)	4⁗′	138.1	-
3″	76.1	3.52 (dd, 8.5, 9.0)	7⁗′	145.2	7.39 (d, 16.0)
4″	69.1	3.27 (dd, 9.0, 9.0)	8⁗′	114.3	6.30 (d, 16.0)
5″	76.2	3.32 (m)	9⁗′	166.4	-
6″	67.8	3.45 (dd, 5.0, 11.5)	3⁗′,5⁗′-OCH_3	55.9	3.77 (s)
		3.78 (br. d, *ca.* 12)			

Apetalumoside B9 (**3**), $[\alpha]_D^{25}$ –61.6° (MeOH). Negative-ion HRESI-TOF-MS determination suggested the molecular formula of it was $C_{55}H_{60}O_{30}$ (*m*/*z* 1199.3095 $[M - H]^-$, calcd for $C_{55}H_{59}O_{30}$ 1199.3097). The

proton and carbon signals in ^{1}H and ^{13}C-NMR spectra (DMSO-d_6, Table 3) were very similar to those of **1**, except for the signals due to the aglycon, quercetin [δ 6.15 (1H, br. s, H-6), 6.20 (1H, br. s, H-8), 6.86 (1H, d, J = 8.5 Hz, H-5′), 7.52 (1H, dd, J = 1.5, 8.5 Hz, H-6′), 7.57 (1H, d, J = 1.5 Hz, H-2′), 12.76 (1H, br. s, 5-OH)]. The linkage positions of sugar parts with aglycon and two sinapoyl groups were elucidated by the HMBC determination (Figure 2), which showed long-range correlations between δ_H 5.69 (1H, d, J = 7.5 Hz, H-1″) and δ_C 132.6 (C-3); δ_H 4.63 (1H, d, J = 7.5 Hz, H-1‴and δ_C 82.6 (C-2″); δ_H 4.27 (1H, d, J = 8.0 Hz, H-1⁗) and δ_C 66.6 (C-6″); δ_H [4.15 (1H, br. d, *ca.* J = 12 Hz), 4.28 (1H, dd, J = 4.5, 11.5 Hz), H$_2$-6‴] and δ_C 166.4 (C-9⁗); δ_H 4.42 (1H, dd, J = 8.0, 9.0 Hz, H-2⁗) and δ_C 165.5 (C-9⁗′). Meanwhile, the badly overlapped protons in sugar chemical shift range were assigned by HSQC-TOCSY experiment. Finally, the presence of D-glucose was proved by acid analysis [1,2]. Then the structure of apetalumoside B$_9$ (**3**) was elucidated as quercetin 3-*O*-[β-D-(2-*O*-sinapoyl)-glucopyranosyl(1→6)]-β-D-(6-*O*-sinapoyl)-glucopyranosyl(1→2)-β-D-glucopyranoside.

Table 3. ^{1}H and ^{13}C-NMR data for **3** in DMSO-d_6 (500 MHz for ^{1}H and 125 MHz for ^{13}C).

No.	δ_C	δ_H (*J* in Hz)	No.	δ_C	δ_H (*J* in Hz)
2	156.0	-	4‴	69.4	3.23 (dd, 8.0, 8.0)
3	132.6	-	5‴	73.8	3.41 (m)
4	177.3	-	6‴	63.1	4.15 (br. d, *ca.* 12)
5	161.0	-			4.28 (dd, 4.5, 11.5)
6	98.7	6.15 (br. s)	1⁗	100.1	4.27 (d, 8.0)
7	163.9	-	2⁗	73.7	4.42 (dd, 8.0, 9.0)
8	93.7	6.20 (br. s)	3⁗	74.2	2.79 (dd, 9.0, 9.0)
9	156.1	-	4⁗	69.6	3.15 (dd, 8.0, 9.0)
10	103.9	-	5⁗	76.3	2.69 (m)
1′	121.0	-	6⁗	60.1	3.44 (m)
2′	116.1	7.57 (d, 1.5)	1⁗′	124.2	-
3′	144.7	-	2⁗′,6⁗′	105.9	6.79 (s)
4′	148.5	-	3⁗′,5⁗′	147.8	-
5′	115.2	6.86 (d, 8.5)	4⁗′	138.1	-
6′	121.6	7.52 (dd, 1.5, 8.5)	7⁗′	145.1	7.34 (d, 16.0)
5-OH	-	12.76 (br. s)	8⁗′	114.3	6.25 (d, 16.0)
1″	97.9	5.69 (d, 7.5)	9⁗′	166.4	-
2″	82.6	3.51 (dd, 7.5, 8.5)	3⁗′,5⁗′-OCH$_3$	55.9	3.74 (s)
3″	76.1	3.39 (dd, 8.0, 8.5)	1⁗″	124.5	-
4″	69.2	3.04 (dd, 8.0, 9.0)	2⁗″,6⁗″	105.9	7.07 (s)
5″	78.1	3.16 (m)	3⁗″,5⁗″	148.1	-
6″	66.6	3.43 (dd, 5.5, 11.5)	4⁗″	138.2	-
		3.69 (br. d, *ca.* 12)	7⁗″	145.1	7.49 (d, 16.0)
1‴	104.2	4.63 (d, 7.5)	8⁗″	115.0	6.32 (d, 16.0)
2‴	74.3	3.14 (dd, 7.5, 8.0)	9⁗″	165.5	-
3‴	76.2	3.24 (dd, 8.0, 8.0)	3⁗″,5⁗″-OCH$_3$	56.2	3.88 (s)

Apetalumoside B$_{10}$ (**4**) was obtained as yellow powder with negative rotation ($[\alpha]_D^{25}$ –66.4°, in MeOH). Acid hydrolysis with 1 M HCl, it gave D-glucose [1,2]. The molecular formula of **4**, $C_{44}H_{50}O_{26}$ (*m*/*z* 993.2537 $[M - H]^-$, calcd for $C_{44}H_{49}O_{26}$ 993.2518), was the same as that of **2**. And the ^{1}H and

^{13}C (DMSO-d_6, Table 4) together with various 2D NMR experiments of **4** showed the same fragments {quercetin aglycon [δ 6.39 (1H, d, J = 1.5 Hz, H-6), 6.58 (1H, d, J = 1.5 Hz, H-8), 6.90 (1H, d, J = 8.5 Hz, H-5′), 7.57 (1H, d, J = 1.5 Hz, H-2′), 7.61 (1H, dd, J = 1.5, 8.5 Hz, H-6′), 12.70 (1H, br. s, 5-OH)], three β-D-glucopyranosyl groups [δ 4.68 (1H, d, J = 7.5 Hz, H-1‴), 5.03 (1H, d, J = 7.5 Hz, H-1⁗), 5.68 (1H, d, J = 6.5 Hz, H-1″)], and a sinapoyl [δ_H 3.75 (6H, s, 3⁗,5⁗-OCH_3), 6.25 (1H, d, J = 15.5 Hz, H-8⁗), 6.78 (2H, s, H-2⁗,6⁗), 7.36 (1H, d, J = 15.5 Hz, H-7⁗); δ_C 166.4 (C-9⁗)]} as **2**. But comparison the ^{1}H and ^{13}C-NMR data of 6–8 positions in **4** [δ_H 6.39 (H-6), 6.58 (H-8); δ_C 94.0 (C-8), 99.1 (C-6), 162.5 (C-7)] with those in **2** [δ_H 6.16 (H-6), 6.26 (H-8); δ_C 93.4 (C-8), 98.6 (C-6), 164.1 (C-7)] revealed a glycoside substitution shift around the 7-position. Meanwhile, the ^{13}C-NMR data of C-6″ of **4** (δ_C 60.4) shifted to high field compared with that of **2** (δ_C 67.8), which meant there was no substitution at C-6″ position for compound **4**. Furthermore, in the HMBC experiment, long-range correlations were observed between δ_H 5.68 (H-1″) and δ_C 133.1 (C-3); δ_H 4.68 (H-1‴) and δ_C 83.6 (C-2″); δ_H 5.03 (H-1⁗) and δ_C 162.5 (C-7); δ_H [4.20 (1H, br. d, *ca.* J = 12 Hz), 4.31 (1H, dd, J = 5.0, 11.5 Hz), H_2-6‴] and δ_C 166.4 (C-9⁗). Consequently, the structure of apetalumoside B_{10} (**4**) was determined as quercetin 3-*O*-β-D-(6-*O*-sinapoyl)-glucopyranosyl(1→2)-β-D-glucopyranoside-7-*O*-β-D-glucopyranoside.

Table 4. ^{1}H and ^{13}C-NMR data for **4** in DMSO-d_6 (500 MHz for ^{1}H and 125 MHz for ^{13}C).

No.	δ_C	δ_H (J in Hz)	No.	δ_C	δ_H (J in Hz)
2	156.1	-	1‴	104.5	4.68 (d, 7.5)
3	133.1	-	2‴	74.4	3.17 (dd, 7.5, 9.0)
4	177.4	-	3‴	76.1	3.26 (dd, 8.0, 9.0)
5	160.7	-	4‴	69.5	3.25 (dd, 8.0, 8.0)
6	99.1	6.39 (d, 1,5)	5‴	73.8	3.53 (m)
7	162.5	-	6‴	63.1	4.20 (br. d, *ca.* 12)
8	94.0	6.58 (d, 1.5)			4.31 (dd, 5.0, 11.5)
9	155.7	-	1⁗	99.6	5.03 (d, 7.5)
10	105.4	-	2⁗	73.0	3.28 (dd, 7.5, 8.0)
1′	120.8	-	3⁗	76.2	3.34 (dd, 8.0, 9.0)
2′	116.2	7.57 (d, 1.5)	4⁗	69.5	3.19 (dd, 9.0, 9.0)
3′	144.8	-	5⁗	77.0	3.44 (m)
4′	148.7	-	6⁗	60.5	3.49 (m, overlapped)
5′	115.2	6.90 (d, 8.5)			3.72 (br. d, *ca.* 11)
6′	121.9	7.61 (dd, 1.5, 8.5)	1⁗	124.1	-
5-OH	-	12.70 (br. s)	2⁗,6⁗	105.8	6.78 (s)
1″	97.7	5.68 (d, 6.5)	3⁗,5⁗	147.8	-
2″	83.6	3.49 (m, overlapped)	4⁗	138.1	-
3″	76.3	3.49 (m, overlapped)	7⁗	145.1	7.36 (d, 15.5)
4″	69.4	3.13 (dd, 8.0, 8.0)	8⁗	114.3	6.25 (d, 15.5)
5″	77.4	3.10 (m)	9⁗	166.4	-
6″	60.4	3.27 (m, overlapped)	3⁗,5⁗-OCH_3	55.9	3.75 (s)
		3.49 (m, overlapped)			

Apetalumoside B11 (**5**) was isolated as yellow powder, too. It had the molecular formula, $C_{50}H_{60}O_{31}$, deduced from the negative-ion HRESI-TOF-MS (*m*/*z* 1155.3063 $[M - H]^-$, calcd for $C_{50}H_{59}O_{31}$ 1155.3046). On acid hydrolysis and identification with HPLC analysis, the presence of D-glucose was determined [1,2]. The ^1H and ^{13}C (DMSO-*d*6, Table 5) together with ^1H ^1H COSY, HSQC, HMBC, and HSQC-TOCSY spectra revealed it had the same aglycon, quercetin as **2**–**4** [δ 6.38 (1H, d, *J* = 2.0 Hz, H-6), 6.55 (1H, d, *J* = 2.0 Hz, H-8), 6.88 (1H, d, *J* = 8.5 Hz, H-5′), 7.57 (1H, d, *J* = 2.0 Hz, H-2′), 7.58 (1H, dd, *J* = 2.0, 8.5 Hz, H-6′), 12.63 (1H, br. s, 5-OH)]. On the other hand, there were four β-D-glucopyranosyl groups [δ 3.99 (1H, d, *J* = 7.5 Hz, H-1‴), 4.66 (1H, d, *J* = 7.5 Hz, H-1″), 5.01 (1H, d, *J* = 7.5 Hz, H-1⁗), 5.62 (1H, d, *J* = 6.5 Hz, H-1″)], and a sinapoyl [δ_H 3.75 (6H, s, 3⁗,5⁗-OCH_3), 6.26 (1H, d, *J* = 16.0 Hz, H-8⁗), 6.80 (2H, s, H-2⁗,6⁗), 7.36 (1H, d, *J* = 16.0 Hz, H-7⁗); δ_C 166.4 (C-9⁗)]} in **5**. There was one more β-D-glucopyranosyl in **5** than in **4**. Moreover, the ^{13}C-NMR data of C-6″ for **5** (δ_C 67.8) shifted to low field compared with that of **4** (δ_C 60.4), which indicated C-6″ position might be substituted with β-D-glucopyranosyl in **5**. Meanwhile, in the HMBC experiment (Figure 3), long-range correlation was observed between δ_H 3.99 (1H, d, *J* = 7.5 Hz, H-1‴) and δ_C 67.8 (C-6″). Finally, in the HSQC-TOCSY spectra, the correlations between δ_C 97.9 (C-1″) and δ_H 3.25 (H-4″), 3.32 (H-5″), 3.50 (H-3″), 3.52 (H-2″), 5.62 (H-1″); δ_H 3.78 (H-6b″) and δ_C 67.8 (C-6″), 69.2 (C-4″), 76.3 (C-5″); δ_C 104.5 (C-1‴) and δ_H 3.16 (H-2‴), 3.25 (H-4‴), 3.26 (H-3‴), 3.51 (H-5‴), 4.66 (H-1‴); δ_H 4.19, 4.30 (H_2-6‴) and δ_C 63.1 (C-6‴), 69.4 (C-4‴), 73.8 (C-5‴); δ_C 103.2 (C-1⁗) and δ_H 2.80 (H-2⁗), 2.85 (H-5⁗), 2.90 (H-3⁗), 2.98 (H-4⁗), 3.99 (H-1⁗); δ_C 60.7 (C-6⁗) and δ_H 2.85 (H-5⁗), 2.90 (H-3⁗), 2.98 (H-4⁗), 3.38, 3.54 (H_2-6⁗); δ_C 99.8 (C-1⁗) and δ_H 3.19 (H-4⁗), 3.32 (H-3⁗), 3.27 (H-2⁗), 3.43 (H-5⁗), 5.01 (H-1⁗); δ_C 60.6 (C-6⁗) and δ_H 3.19 (H-4⁗), 3.32 (H-3⁗), 3.43 (H-5⁗), 3.49, 3.72 (H_2-6⁗) were observed, then the badly overlapped protons in sugar chemical shift range were assigned clearly. On the basis of above mentioned evidence, the structure of **5** was determined to be quercetin 3-*O*-[β-D-glucopyranosyl(1→6)]-β-D-(6-*O*-sinapoyl)-glucopyranosyl(1→2)-β-D-glucopyranoside-7-*O*-β-D-glucopyranoside.

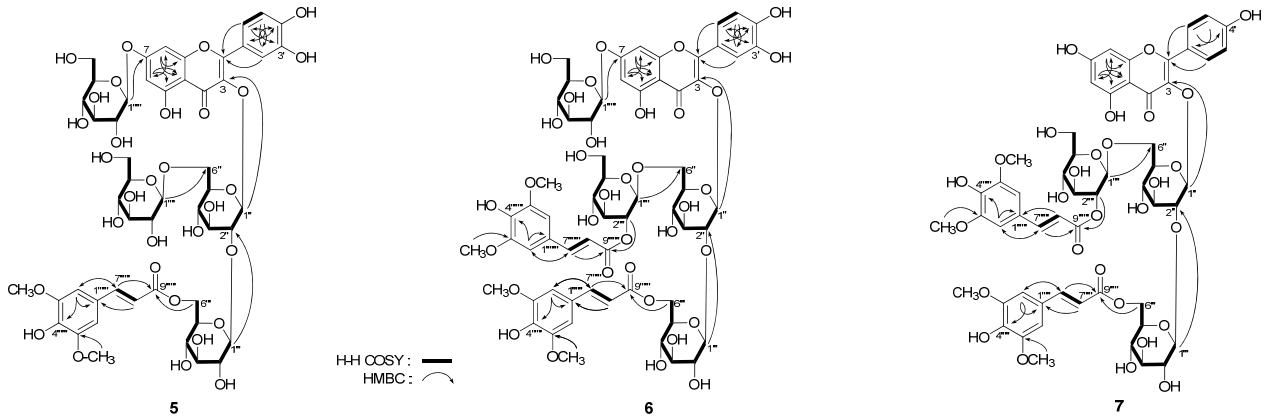


Figure 3. The main ^1H ^1H COSY and HMBC correlations of **5**–**7**.

Table 5. ^{1}H and ^{13}C-NMR data for **5** in DMSO-d_6 (500 MHz for ^{1}H and 125 MHz for ^{13}C).

No.	δ_C	δ_H (*J* in Hz)	No.	δ_C	δ_H (*J* in Hz)
2	156.2	-	4‴	69.4	3.25 (m, overlapped)
3	133.1	-	5‴	73.8	3.51 (m)
4	177.3	-	6‴	63.1	4.19 (br. d, *ca.* 12)
5	160.7	-			4.30 (dd, 4.5, 12.0)
6	99.2	6.38 (d, 2.0)	1⁗	103.2	3.99 (d, 7.5)
7	162.6	-	2⁗	73.1	2.80 (dd, 7.5, 8.0)
8	94.3	6.55 (d, 2.0)	3⁗	76.2	2.90 (dd, 8.0, 9.0)
9	155.7	-	4⁗	69.6	2.98 (dd, 9.0, 9.0)
10	105.5	-	5⁗	76.4	2.85 (m)
1′	120.8	-	6⁗	60.7	3.38 (dd, 5.5, 11.5)
2′	116.3	7.57 (d. 2.0)			3.54 (br. d, *ca.* 12)
3′	144.8	-	1⁗′	99.8	5.01 (d, 7.5)
4′	148.7	-	2⁗′	73.1	3.27 (dd, 7.5, 8.0)
5′	115.2	6.88 (d, 8.5)	3⁗′	76.2	3.32 (dd, 8.0, 9.0)
6′	121.9	7.58 (dd, 2.0, 8.5)	4⁗′	69.5	3.19 (dd, 9.0, 9.0)
5-OH	-	12.63 (br. s)	5⁗′	77.0	3.43 (m)
1″	97.9	5.62 (d, 6.5)	6⁗′	60.6	3.49 (dd, 4.0, 11.5)
2″	83.2	3.52 (dd, 6.5, 8.0)			3.72 (br. d, *ca.* 12)
3″	76.1	3.50 (dd, 8.0, 8.0)	1⁗″	124.2	-
4″	69.2	3.25 (m, overlapped)	2⁗″,6⁗″	105.9	6.80 (s)
5″	76.3	3.32 (m)	3⁗″,5⁗″	147.8	-
6″	67.8	3.43 (dd, 5.5, 11.5)	4⁗″	138.1	-
		3.78 (dd, 3.5, 11.5)	7⁗″	145.1	7.36 (d, 16.0)
1‴	104.5	4.66 (d, 7.5)	8⁗″	114.3	6.26 (d, 16.0)
2‴	74.4	3.16 (dd, 7.5, 8.0)	9⁗″	166.4	-
3‴	76.2	3.26 (m, overlapped)	3⁗″,5⁗″-OCH_3	55.9	3.75 (s)

Apetalumoside B$_{12}$ (**6**), $[\alpha]_D^{25}$ –84.0° (MeOH), was isolated as yellow powder. The molecular formula, $C_{61}H_{70}O_{35}$, of **6** was determined from negative-ion HRESI-TOF-MS (*m*/*z* 1361.3625 $[M-H]^-$, calcd for $C_{61}H_{69}O_{35}$ 1361.3625). Acid hydrolysis of **6** with 1 M HCl liberated D-glucose [1,2]. Comparison the ^{1}H and ^{13}C (DMSO-d_6, Table 6) spectra with those of **5**, revealed there was another sinapoyl [δ_H 3.87 (6H, s, 3⁗″,5⁗″-OCH_3), 6.32 (1H, d, *J* = 16.0 Hz, H-8⁗″), 7.06 (2H, s, H-2⁗″,6⁗″), 7.50 (1H, d, *J* = 16.0 Hz, H-7⁗″); δ_C 165.5 (C-9⁗″)] appeared in **6**, and the ^{1}H-NMR data of 2‴-position [δ_H 4.39 (1H, dd, *J* = 8.0, 8.0 Hz, H-2‴)] shifted to low field relatived to that of **5** [δ_H 2.80 (1H, dd, *J* = 7.5, 8.0 Hz, H-2‴). The above mentioned evidence suggested the another sinapoyl group linked with 2⁗-position, which was certified by the long-range correlation between δ_H 4.39 (H-2⁗) and δ_C 165.5 (C-9⁗″) observed in the HMBC experiment. In conjunction with analysis of HSQC and HSQC-TOCSY spectra, the ^{1}H and ^{13}C-NMR data for **6** were assigned. Finally, the structure of apetalumoside B_{12} (**6**) was clarified to be quercetin 3-*O*-[β-D-(2-*O*-sinapoyl)-glucopyranosyl(1→6)]-β-D-(6-*O*-sinapoyl)-glucopyranosyl(1→2)-β-D-glucopyranoside-7-*O*-β-D-glucopyranoside.

Table 6. ^{1}H and ^{13}C-NMR data for **6** in DMSO-d_6 (500 MHz for ^{1}H and 125 MHz for ^{13}C).

No.	δ_C	δ_H (*J* in Hz)	No.	δ_C	δ_H (*J* in Hz)
2	156.8	-	1‴′	100.2	4.22 (d, 8.0)
3	132.8	-	2‴′	73.4	4.39 (dd, 8.0, 8.0)
4	177.4	-	3‴′	74.0	2.71 (dd, 8.0, 8.0)
5	160.8	-	4‴′	69.6	3.11 (dd, 8.0, 9.5)
6	99.3	6.40 (d, 1.5)	5‴′	76.3	2.68 (m)
7	162.7	-	6‴′	60.1	3.44 (m, overlapped)
8	94.8	6.51 (d, 1.5)			3.48 (m, overlapped)
9	155.5	-	1⁗	100.0	5.00 (d, 7.5)
10	105.5	-	2⁗	73.1	3.26 (dd, 7.5, 7.5)
1′	120.7	-	3⁗	76.2	3.30 (dd, 7.5, 8.5)
2′	116.3	7.58 (d, 1.5)	4⁗	69.6	3.16 (dd, 7.5, 8.5)
3′	144.8	-	5⁗	77.0	3.40 (m)
4′	148.8	-	6⁗	60.6	3.48 (m, overlapped)
5′	115.2	6.86 (d, 8.5)			3.75 (br. d, *ca.* 12)
6′	121.7	7.51 (dd, 1.5, 8.5)	1‴″	124.1	-
5-OH	-	12.76 (br. s)	2‴″,6‴″	105.8	6.76 (s)
1″	97.8	5.67 (d, 7.5)	3‴″,5‴″	147.8	-
2″	82.8	3.48 (m, overlapped)	4‴″	138.1	-
3″	76.0	3.38 (dd, 7.5, 8.0)	7‴″	145.2	7.33 (d, 16.0)
4″	69.1	3.01 (dd, 8.0, 9.0)	8‴″	114.3	6.22 (d, 16.0)
5″	78.1	3.14 (m)	9‴″	166.3	-
6″	66.7	3.45 (m, overlapped)	3‴″,5‴″-OCH_3	55.9	3.73 (s)
		3.67 (br. d, *ca.* 13)	1⁗″	124.5	-
1‴	104.4	4.61 (d, 7.5)	2⁗″,6⁗″	105.9	7.06 (s)
2‴	74.4	3.13 (dd, 7.5, 8.0)	3⁗″,5⁗″	148.1	-
3‴	76.2	3.24 (dd, 8.0, 8.0)	4⁗″	138.2	-
4‴	69.5	3.23 (dd, 8.0, 8.0)	7⁗″	145.1	7.50 (d, 16.0)
5‴	73.8	3.41 (m)	8⁗″	114.9	6.32 (d, 16.0)
6‴	63.2	4.15 (br. d, *ca.* 11)	9⁗″	165.5	-
		4.28 (dd, 6.5, 11.0)	3⁗″,5⁗″-OCH_3	56.1	3.87 (s)

Apetalumoside C1 (**7**), $[\alpha]_D^{25}$ –47.2° (MeOH). Negative-ion HRESI-TOF-MS determination suggested the molecular formula of it was $C_{55}H_{60}O_{29}$ (*m*/*z* 1183.3123 $[M - H]^-$, calcd for $C_{55}H_{59}O_{29}$ 1183.3147). Treated **7** with 1 M HCl to yield D-glucose [1,2]. The proton and carbon signals in ^{1}H and ^{13}C-NMR spectra (DMSO-d_6, Table 7) were very similar to those of **1**, except for the signals due to the aglycon, kaempferol [δ 6.14 (1H, br. s, H-6), 6.27 (1H, br. s, H-8), 6.85 (2H, d, *J* = 8.5 Hz, H-3′,5′), 7.93 (2H, d, *J* = 8.5 Hz, H-2′,6′), 12.72 (1H, br. s, 5-OH)]. The linkage positions of sugar parts with aglycon and two sinapoyl groups were determined by the HMBC experiment, which showed long-range correlations between δ_H 5.58 (1H, d, *J* = 6.5 Hz, H-1″) and δ_C 132.5 (C-3); δ_H 4.62 (1H, d, *J* = 7.5 Hz, H-1‴) and δ_C 82.0 (C-2″); δ_H 4.26 (1H, d, *J* = 8.0 Hz, H-1⁗) and δ_C 66.7 (C-6″); δ_H [4.17 (1H, br. d, *ca.* *J* = 12 Hz), 4.28 (1H, dd, *J* = 5.5, 11.5 Hz), H_2-6‴] and δ_C 166.4 (C-9⁗); δ_H 4.43 (1H, dd, *J* = 8.0, 9.0 Hz, H-2⁗) and δ_C 165.4 (C-9⁗″). Moreover, the ^{1}H-NMR data for four β-D-glucopyranosyl groups were assigned by HSQC and HSQC-TOCSY determination. On the basis of above mentioned evidence, the structure

of apetalumoside C_1 (**7**) was elucidated as kaempferol 3-*O*-[β-D-(2-*O*-sinapoyl)-glucopyranosyl(1→6)]-β-D-(6-*O*-sinapoyl)-glucopyranosyl(1→2)-β-D-glucopyranoside.

Table 7. ^{1}H and ^{13}C-NMR data for **7** in DMSO-d_6 (500 MHz for ^{1}H and 125 MHz for ^{13}C).

No.	δ_C	δ_H (*J* in Hz)	No.	δ_C	δ_H (*J* in Hz)
2	156.1	-	6‴	63.2	4.17 (br. d, *ca.* 12)
3	132.5	-			4.28 (dd, 5.5, 11.5)
4	177.3	-	1⁗	100.2	4.26 (d, 8.0)
5	161.1	-	2⁗	73.6	4.43 (dd, 8.0, 9.0)
6	98.9	6.14 (br. s)	3⁗	74.2	2.86 (dd, 9.0, 9.0)
7	164.5	-	4⁗	69.9	3.11 (dd, 9.0, 9.0)
8	93.8	6.27 (br. s)	5⁗	76.5	2.78 (m)
9	156.2	-	6⁗	60.4	3.40 (m, overlapped)
10	103.7	-			3.52 (br. d, *ca.* 12)
1′	120.6	-	1⁗′	124.2	-
2′,6′	130.7	7.93 (d, 8.5)	2⁗′,6⁗′	106.0	6.79 (s)
3′,5′	115.1	6.85 (d, 8.5)	3⁗′,5⁗′	147.8	-
4′	159.9	-	4⁗′	138.2	-
5-OH	-	12.72 (br. s)	7⁗′	145.1	7.37 (d, 15.5)
1″	97.9	5.58 (d, 6.5)	8⁗′	114.4	6.27 (d, 15.5)
2″	82.0	3.41 (dd, 6.5, 8.0)	9⁗′	166.4	-
3″	76.2	3.40 (dd, 8.0, 9.0)	3⁗′,5⁗′-OCH_3	55.9	3.73 (s)
4″	69.2	3.01 (dd, 9.0, 9.0)	1⁗″	124.5	-
5″	77.8	3.13 (m)	2⁗″,6⁗″	106.0	7.05 (s)
6″	66.7	3.44 (dd, 6.5, 12.0)	3⁗″,5⁗″	148.1	-
		3.68 (br. d, *ca.* 12)	4⁗″	138.3	-
1‴	103.9	4.62 (d, 7.5)	7⁗″	145.1	7.49 (d, 16.0)
2‴	74.3	3.11 (dd, 7.5, 9.0)	8⁗″	115.0	6.29 (d, 16.0)
3‴	76.3	3.21 (dd, 9.0, 9.0)	9⁗″	165.4	-
4‴	69.5	3.23 (dd, 9.0, 9.0)	3⁗″,5⁗″-OCH_3	56.1	3.87 (s)
5‴	73.8	3.35 (m)			

3. Experimental

3.1. General

UV spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer (Varian, Inc., Hubbardsdon, MA, USA). IR spectra were obtained on a Varian 640-IR FT-IR spectrophotometer (Varian Australia Pty Ltd, Mulgrave, Australia). Optical rotations were determined on a Rudolph Autopol® IV automatic polarimeter (Rudolph Research Analytical, Hackettstown NJ, USA). NMR spectra were measured on a Bruker AVANCE III 500 MHz NMR spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C-NMR, Bruker BioSpin AG Industriestrasse 26 CH-8117, Fällanden, Switzerland) with TMS as an internal standard. Negative-ion HRESI-TOF-MS were determined on an Agilent 6520 Accurate-Mass Q-Tof MS spectrometer (drying gas, N_2; flow rate, 8.0 L/min; temperature, 350 °C; nebulizer, 30 psig; capillary, −3500 V;

fragmentor, 175 V; skimmer, 65 V; OCT RF V, 750 V. Mass range recorded *m*/*z* 100–1200, Agilent Technologies, Inc., Santa Clara, CA, USA).

Column chromatographies were performed on macroporous resin D101 (Haiguang Chemical Co., Ltd., Tianjin, China), Silica gel (48–75 μm, Qingdao Haiyang Chemical Co., Ltd., Qingdao, China), ODS (40–63 μm, YMC Co., Ltd., Tokyo, Japan), and Sephadex LH-20 (Ge Healthcare Bio-Sciences, Uppsala, Sweden), and Preparative HPLC (PHPLC) column, Cosmosil 5C18-MS-II (20 mm i.d. × 250 mm, 5 μM, Nakalai Tesque, Inc., Tokyo, Japan) were used to purify the constituents.

3.2. Plant Material

The seeds of *L. apetalum* were collected from Anguo city, China, and identified by Li Tianxiang. The voucher specimen was deposited at the Academy of Traditional Chinese Medicine of Tianjin University of TCM (No. 20120501).

3.3. Extraction and Isolation

L. apetalum seeds (10 kg) were crushed and refluxed with 50% ethanol/water. Then, the 50% ethanol/water extract was partitioned in a $CHCl_3/H_2O$ mixture (1:1, *v*/*v*), and $CHCl_3$ and H_2O layers were obtained. Then the H_2O layer was subjected to D101 macroporous resin CC (H_2O → 95% EtOH). As a result, H_2O and 95% EtOH eluted fractions were given.

The EtOH fraction (80 g) was subjected to silica gel CC [$CHCl_3$ → $CHCl_3$/MeOH (100:3 → 100:5, *v*/*v*) → $CHCl_3$/MeOH/H_2O (10:3:1 → 6:4:1, *v*/*v*/*v*) → MeOH] to yield 16 fractions (Fr. 1–16). Fraction 12 was isolated by ODS CC [MeOH/H_2O (10:90 → 20:80 → 30:70 → 40:60 → 50:50 → 70:30→ 100:0, *v*/*v*] to give 9 fractions (Fr. 12-1–12-9). Fraction 12-6 was separated by PHPLC [CH_3CN/1% CH_3COOH (18:82 → 100:0, *v*/*v*)] to obtain 14 fractions (Fr. 12-6-1–12-6-14). Fraction 12-6-11 was purified by PHPLC [CH_3CN/1% CH_3COOH (20:80, *v*/*v*)], and apetalumoside B_9 (**3**, 16.1 mg) was obtained. Fraction 12-6-12 was isolated by PHPLC [CH_3CN/1% CH_3COOH (18:82, *v*/*v*)] to yield apetalumosides A_1 (**1**, 23.7 mg) and C_1 (**7**, 15.6 mg) respectively. Fraction 14 was separated by Sephadex LH-20 CC [MeOH/H_2O (1:1, *v*/*v*)] to yield 7 fractions (Fr. 14-1–14-7). Fraction 14-5 was purified by PHPLC [CH_3CN/1% CH_3COOH (15:85, *v*/*v*)], as a result, 18 fractions (Fr. 14-5-1–14-5-18) were obtained. Fraction 14-5-5 was subjected to PHPLC [CH_3CN/1% CH_3COOH (14:86, *v*/*v*)] to give apetalumoside B_{12} (**6**, 11.4 mg). Fraction 14-5-7 was separated by Sephadex LH-20 CC [MeOH/H_2O (1:1, *v*/*v*)] to afford three fractions (Fr. 14-5-7-1–14-5-7-3). Fraction 14-5-7-2 was subjected to PHPLC [CH_3CN/1% CH_3COOH (12:88, *v*/*v*)], and apetalumoside B_{10} (**4**, 19.8 mg) was obtained. Fraction 14-5-15 was further separated by PHPLC [MeOH/1% CH_3COOH (34:66, *v*/*v*)] to give apetalumoside B_8 (**2**, 50.2 mg). Fraction 16 was separated by PHPLC through gradient elution [MeOH/1% CH_3COOH (20:80 → 25:75 → 30:70 → 35:65 → 40:60 → 50:50 → 60:40 → 100:0, *v*/*v*)] to obtain 26 fractions (Fr. 16-1–16-26). Fraction 16-10 was further isolated by PHPLC [CH_3CN/1% CH_3COOH (12:88, *v*/*v*)] to yield three fractions (Fr. 16-10-1–16-10-3). Fraction 16-10-2 was purified by Sephadex LH-20 CC [MeOH/H_2O (1:1, *v*/*v*)], and apetalumoside B_{11} (**5**, 16.8 mg) was given.

Apetalumoside A1 (**1**): Yellow powder. $[\alpha]_D^{25}$ –49.0° (*c* = 0.97, MeOH); IR ν_{max} (KBr) cm^{-1}: 3394, 2933, 1701, 1648, 1630, 1604, 1514, 1458, 1356, 1284, 1175, 1114, 1075, 826; UV λ_{max} (MeOH) nm (log ε):

329 (4.56), 266 (4.26, sh), 236 (4.56). ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectroscopic data, see Table 1. HRESI-TOF-MS: Negative-ion mode *m*/*z* 1213.3238 $[M - H]^-$ (calcd for $C_{56}H_{61}O_{30}$ 1213.3253).

Apetalumoside B8 (**2**): Yellow powder. $[\alpha]_D^{25}$ –41.6° (*c* = 0.99, MeOH); IR ν_{max} (KBr) cm^{-1}: 3367, 2936, 1700, 1650, 1628, 1606, 1514, 1456, 1361, 1287, 1196, 1077, 823, 597, 521; UV λ_{max} (MeOH) nm (log ε): 334 (4.40), 266 (4.22, sh), 241 (4.38). ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectroscopic data, see Table 2. HRESI-TOF-MS: Negative-ion mode *m*/*z* 993.2522 $[M - H]^-$ (calcd for $C_{44}H_{49}O_{26}$ 993.2518).

Apetalumoside B9 (**3**): Yellow powder. $[\alpha]_D^{25}$ –61.6° (*c* = 0.98, MeOH); IR ν_{max} (KBr) cm^{-1}: 3394, 2942, 1700, 1650, 1631, 1605, 1514, 1457, 1362, 1285, 1173, 1115, 1077, 827; UV λ_{max} (MeOH) nm (log ε): 329 (4.60), 269 (4.26, sh), 238 (4.57). ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectroscopic data, see Table 3. HRESI-TOF-MS: Negative-ion mode *m*/*z* 1199.3095 $[M - H]^-$ (calcd for $C_{55}H_{59}O_{30}$ 1199.3097).

Apetalumoside B10 (**4**): Yellow powder. $[\alpha]_D^{25}$ –66.4° (*c* = 0.98, MeOH); IR ν_{max} (KBr) cm^{-1}: 3366, 2925, 1698, 1652, 1628, 1601, 1515, 1456, 1342, 1283, 1200, 1075, 824; UV λ_{max} (MeOH) nm (log ε): 333 (4.34), 269 (4.20, sh), 242 (4.36). ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectroscopic data, see Table 4. HRESI-TOF-MS: Negative-ion mode *m*/*z* 993.2537 $[M - H]^-$ (calcd for $C_{44}H_{49}O_{26}$ 993.2518).

Apetalumoside B11 (**5**): Yellow powder. $[\alpha]_D^{25}$ –47.6° (*c* = 0.10, MeOH); IR ν_{max} (KBr) cm^{-1}: 3367, 2923, 1702, 1652, 1633, 1601, 1515, 1456, 1343, 1284, 1199, 1075, 824; UV λ_{max} (MeOH) nm (log ε): 333 (4.44), 268 (4.32, sh), 241 (4.45). ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectroscopic data, see Table 5. HRESI-TOF-MS: Negative-ion mode *m*/*z* 1155.3063 $[M - H]^-$ (calcd for $C_{50}H_{59}O_{31}$ 1155.3046).

Apetalumoside B12 (**6**): Yellow powder. $[\alpha]_D^{25}$ –84.0° (*c* = 0.99, MeOH); IR ν_{max} (KBr) cm^{-1}: 3367, 2924, 1700, 1654, 1631, 1600, 1515, 1457, 1342, 1281, 1176, 1073, 825; UV λ_{max} (MeOH) nm (log ε): 330 (4.52), 270 (4.24, sh), 238 (4.50). ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectroscopic data, see Table 6. HRESI-TOF-MS: Negative-ion mode *m*/*z* 1361.3625 $[M - H]^-$ (calcd for $C_{61}H_{69}O_{35}$ 1361.3625).

Apetalumoside C1 (**7**): Yellow powder. $[\alpha]_D^{25}$ –47.2° (*c* = 0.77, MeOH); IR ν_{max} (KBr) cm^{-1}: 3391, 2936, 1700, 1654, 1628, 1606, 1514, 1457, 1360, 1283, 1178, 1114, 1076, 831; UV λ_{max} (MeOH) nm (log ε): 325 (4.47), 265 (4.20), 238 (4.44, sh). ^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) spectroscopic data, see Table 7. HRESI-TOF-MS: Negative-ion mode *m*/*z* 1183.3123 $[M - H]^-$ (calcd for $C_{55}H_{59}O_{29}$ 1183.3147).

Acid Hydrolysis of **1**–**7**: A solution of **1**–**7** (each 1.5 mg) in 1 M HCl (1 mL) was heated under reflux for 3 h, respectively. The reaction mixture was dealt, then analyzed by CH_3CN/H_2O (70:30, *v*/*v*; flow rate 1.0 mL/min) using the same condition as reference [1]. As result, D-glusose was detected from **1**–**7** by comparison of its retention time and optical rotation with that of authentic sample (t_R 8.8 min, positive).

4. Conclusions

As results, seven new sinapoyl acylated flavonoid glycosides were obtained from *L. apetalum* seeds. Although various acylated flavonol glycosides distribute widely in the plant kingdom, sinapoylates such as the flavonoid glycosides reported in this paper are quite rare, which were found only in 21 species from eight family plants, including Cruciferae [3–13], Leguminosae [14,15], Apocynaceae [16], Solanaceae [17], Elaeagnaceae [18,19], Rubiaceae [20,21], Ranunculaceae [22], and Moraceae [23] until now. And almost of them were obtained from the Cruciferae family, which includes *L. apetalum* researched by our lab. This will have some guidance for plant taxonomy.

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Author Contributions

Yi Zhang and Tao Wang designed the research; Pingping Shi, Yongzhe Dong, Tingting Wang, and Xiaoxia Li performed the experimental work; Lifeng Han wrote the manuscript; Jia Hao perfected language. All authors discussed, edited and approved the final version.

Conflicts of Interest

The authors declare no conflict of interest.

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Sample Availability: Samples of all the compounds are available from the authors.