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Flavonoids from *Stellera chamaejasme*

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Abstract

A new flavonoid, 3-[1-[[3-di(4-hydroxyphenyl)methyl]2,4,6-trihydroxyphenyl]3-di(4-hydroxyphenyl)1-propanone-2-yl]5,7-dihydroxy-4H-1-benzopyran-4-one, named mohsenone was isolated from the root of *Stellera chamaejasme* together with chamaechromone and (−)-epiafzelechin 7-O-β-D-glucopyranoside and their structures were elucidated by spectral analyses.

Keywords: *Stellera chamaejasme*; Thymelaeaceae; Root; Mohsenone; Chamaechromone; (−)-Epiafzelechin 7-O-β-D-glucopyranoside; Flavonoids

1. Introduction

The root of the toxic plant, *Stellera chamaejasme* L. (Thymelaeaceae) is used in traditional Chinese medicine as Langdu. From the 80% ethanol extract of the root three flavonoids, named mohsenone (**1**), chamaechromone (**2**) and (−)-epiafzelechin 7-O-β-D-glucopyranoside (**3**), were isolated. Their structures were elucidated mainly on the basis of their 1D and 2D NMR spectroscopic data. Compound **1**, named mohsenone, is a new natural product.

2. Results and discussion

The elemental composition of **1** was shown by high-resolution mass spectroscopy to be $C_{43}H_{32}O_{12}$ (*m/z* 739.1845 $[M-1]^+$, $C_{43}H_{31}O_{12}$, calculated 739.1816; *m/z* 741.1960 $[M+1]^+$, $C_{43}H_{33}O_{12}$, calculated 741.1972). The ion at *m/z* 541 can be explained by cleavage of a di-4-hydroxyphenylmethyl group.

The ^{1}H NMR spectrum indicated the presence of a pair of coupled methine protons [δ 6.48 (1H, d, $J = 11.82$ Hz, H-12); 4.64 (1H, d, $J = 11.82$ Hz, H-11)], an isolated methine proton [δ 5.77 (1H, s, H-32)], four units of 4-hydroxyphenyl protons (16 protons at δ 6.60–7.17, each with doublet splitting, $J = 8.18$–8.52 Hz). The protons at δ 6.18 (1H, d, $J = 2.17$ Hz, H-6), 6.29 (1H, d, $J = 2.17$ Hz, H-8) and 8.17 (1H, s, H-2) suggest the presence of a unit of 5,7-dihydroxylchromone.

The ^{13}C signal assignments and the C–H correlations were detected via ^1J(C, H) and ^{2-4}J(C, H) by one- and two-dimensional NMR spectroscopic methods, including ATP, HMQC and HMBC experiments. Those ambiguous signals were clarified and reconfirmed by HETCOR and INEPT experiments.

The connectivities of the two bis-4-hydroxyphenylmethine groups with the chromone-2-acetophenone were detected mainly by the HMQC and HMBC experiments. The correlation of protons resonating at δ 6.48 (1H, d, $J = 11.82$ Hz, H-12) and 4.64 (1H, d, $J = 11.82$ Hz, H-11) with carbons whose signals appear at δ 134.75 (C-20) and 135.27 (C-26) suggest that one of the bis-4-hydroxyphenylmethine groups is connected to C-12; the correlation of ^{1}H at 5.77 (1H, s, H-32) with ^{13}C at 111.51 (C-16) and 96.54 (C-18) suggest that another bis-4-hydroxyphenylmethine group is connected to C-16. Those connectivities were reconfirmed by INEPT experiment. In addition, the structural determination of **1** also was done by comparison to compound **2**.

The ESMS showed the molecular weight of **2** to be 542 (*m/z* 543.0 $[M+1]^+$; *m/z* 564.9 $[M+Na]^+$). The high-resolution mass spectrum gave fragments at: *m/z* 199.0753 ($C_{13}H_{11}O_2$) and *m/z* 344.0531 ($C_{17}H_{12}O_8$),

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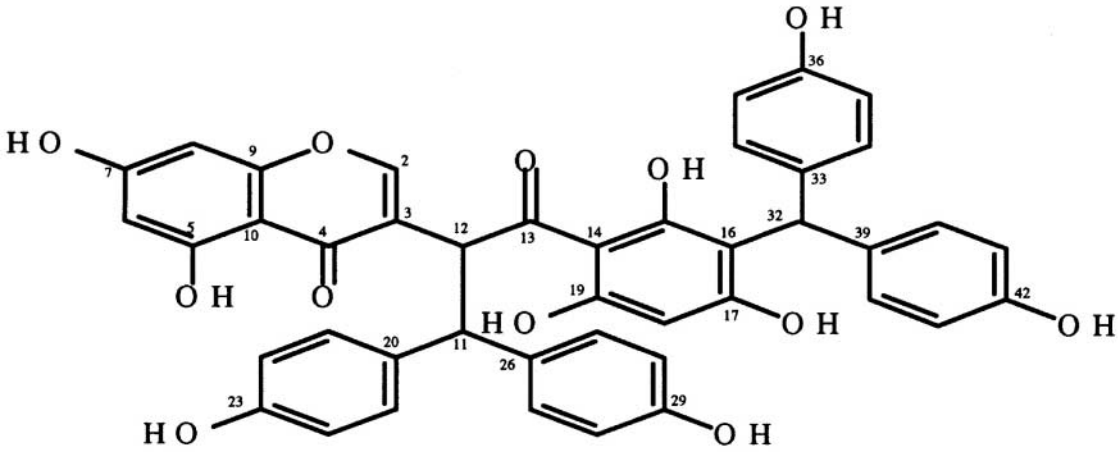
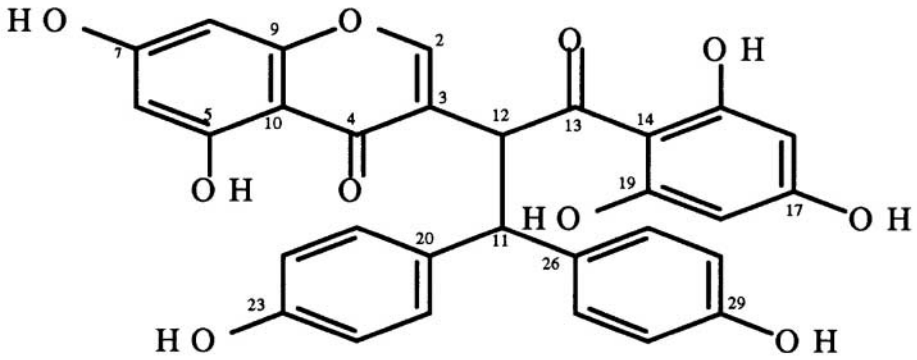
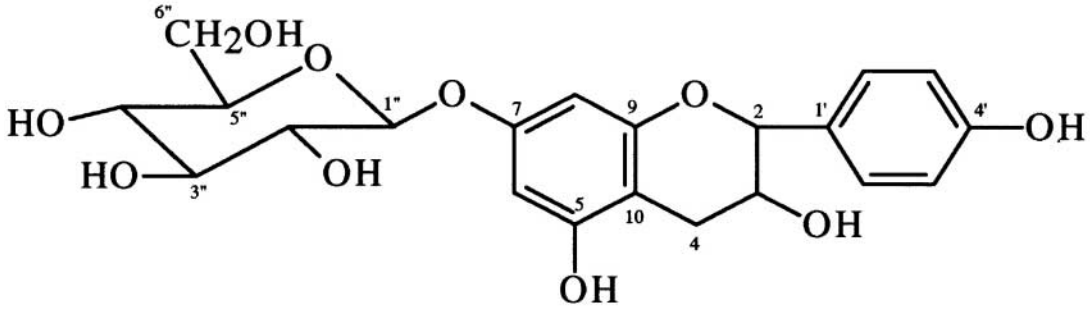


Mohsenone



Chamaechromone



(-)-epiafzelechin 7-O-β-D-glucopyranoside

which can be explained by fragmentation of the bis-4-hydroxyphenylmethane moiety.

The ^{1}H and ^{13}C NMR spectral data of **2** are identical to those of chamaechromone. The assignment was reconfirmed by HMQC and HMBC experiments. The HMQC spectrum suggests the ^{1}H at δ 4.72 (1H, d, $J = 11.90$ Hz, H-11) is attached to δ 54.15 ^{13}C and the ^{1}H at δ 6.55 (1H, d, $J = 11.90$ Hz, H-12) is attached to δ 48.40 ^{13}C. The HMBC spectrum also showed the proton at δ 4.72 (H-11) has ^{2-3}J(C, H) correlation with the carbons at δ 48.40 (C-12), 129.63 (C-27, 31), 130.50 (C-21, 25), 134.70 (C-20) and 135.59 (C-26). The proton at δ 6.55 (H-12), however has the ^{20-3}J correlation with carbons at δ 54.15 (C-11), 121.80 (C-3), 134.70 (C-20), 135.59 (C-26), 181.10 (C-4), 204.23 (C-13), indicating that δ 54.15 signal is assignable to C-11, while δ 48.40 relates to C-12, in contrast to previous literature assignments (Niwa, Liu, Tatematsu, & Hirata, 1984).

The low-resolution POSFAB mass spectrum showed the molecular weight of **3** to be 436.3. The ^{1}H and ^{13}C NMR spectra revealed an aglycone moiety of (–)-

Table 1
^{13}C and ^{1}H NMR data of compound **1** and **2** (500 MHz, acetone-d_6)

	Compound **1**		Compound **2**	
Position	^{13}C	^{1}H	^{13}C	^{1}H
2	157.60	8.17 (1H, s)	156.97	8.15 (1H, s)
3	121.90		121.80	
4	181.60		181.10	
5	163.25		163.23	
6	100.02	6.18 (1H, d, $J = 2.17$ Hz)	99.78	6.16 (1H, d, $J = 2.15$ Hz)
7	165.26		165.73	
8	94.57	6.29 (1H, d, $J = 2.17$ Hz)	94.36	6.27 (1H, d, $J = 2.15$ Hz)
9	158.67		158.49	
10	105.35		105.32	
11	54.05	4.64 (1H, d, $J = 11.82$ Hz)	54.15	4.72 (1H, d, $J = 11.90$ Hz)
12	48.53	6.48 (1H, d, $J = 11.82$ Hz)	48.40	6.55 (1H, d, $J = 11.90$ Hz)
13	204.45		204.23	
14	107.02		106.26	
15	164.53		164.91	
16	111.51	96.12	5.84(1H, s)	
17	163.89		165.17	
18	96.54	5.97 (1H, s)	96.12	5.84 (1H, s)
19	161.39		164.91	
20	134.75		134.70	
21[a]	129.72	7.17 (1H, d, $J = 8.52$ Hz)	130.50	7.13 (1H, d, $J = 8.60$ Hz)
22[b]	115.40	6.66 (1H, d, $J = 8.52$ Hz)	115.58	
23[c]	156.17		156.42	
24[b]	115.40	6.66 (1H, d, $J = 8.52$ Hz)	115.58	
25[a]	129.72	7.17 (1H, d, $J = 8.52$ Hz)	130.50	7.13 (1H, d, $J = 8.60$ Hz)
26	135.27		135.59	
27[a]	130.38	7.14 (1H, d, $J = 8.52$ Hz)	129.63	7.23 (1H, d, $J = 8.60$ Hz)
28[b]	115.40	6.67 (1H, d, $J = 8.52$ Hz)	115.72	
29[c]	156.62		156.38	
30[b]	115.40	6.67 (1H, d, $J = 8.52$ Hz)	115.72	
31[a]	130.38	7.14 (1H, d, $J = 8.52$ Hz)	129.63	7.23 (1H, d, $J = 8.60$ Hz)
32	44.18	5.77 (1H, s)		
33[e]	135.77			
34[d]	130.86	6.98 (1H, d, $J = 8.18$ Hz)		
35	115.85	6.60 (1H, d, $J = 8.18$ Hz)		
36	156.62?			
37	115.85	6.60 (1H, d, $J = 8.18$ Hz)		
38[d]	130.86	6.98 (1H, d, $J = 8.18$ Hz)		
39[e]	135.31			
40[d]	130.86	6.99 (1H, d, $J = 8.18$ Hz)		
41	115.85	6.60 (1H, d, $J = 8.18$ Hz)		
42	156.62?			
43	115.85	6.60 (1H, d, $J = 8.18$ Hz)		
44[d]	130.86	6.99 (1H, d, $J = 8.18$ Hz)		

[a], [b], [c], [d] or [e]: signals may be interchangeable.

epiafzelechin attached by a β-D-glucose. The position of the glucosyl linkage was investigated by HMBC experiment. The ^3J coupling between H-1″ and C-7 suggests the compound to be (−)-epiafzelechin-7-β-D-glucopyranoside (Dhaon, Jian, Sarin, & Khanna, 1989).

The ^1H and ^{13}C signal assignments of **3** were mainly made by H,H-COSY, HMQC and HMBC experiments.

3. Experimental

The NMR spectra were recorded on Varian NMR Unity 500 MHz. Chemical shifts are given in δ (ppm). HPLC was carried out on a Supelcosil LC-18 (10×250 mm) column with UV detector on Waters LC Module I.

3.1. Extraction and isolation

Dried roots of *S. chamaejasme* L. (10 kg), collected on June 7, 1993, in Daqing, China, were extracted with 80% EtOH. The extract was condensed under reduced pressure and the residue was suspended in H_2O. The suspension was extracted with Et_2O and *n*-BuOH, successively. The Et_2O fraction residue (15 g) was chromatographed on a Sephadex LH20 column eluted with MeOH–H_2O 1:3 to 100% MeOH gradient and the subsequent fractions were loaded onto a C-18 column on HPLC and eluted with MeCN–H_2O to give **1** (6 mg) and **2** (30 mg), respectively. The *n*-BuOH-soluble fraction residue (20 g) was chromatographed on a Sephadex G15 column, eluted with MeOH–H_2O 1:3 to 2:1 gradient and then loaded onto a C-18 column on HPLC, 5–30% MeCN–H_2O gradient, to give **3** (15 mg).

3.2. 3-[1-[[3-Di(4-hydroxyphenyl)methyl]2,4,6-trihydroxyphenyl]3-di(4-hydroxyphenyl)1-propanone-2-yl]5,7-dihydroxy-4H-1-benzopyran-4-one (*1*)

Brown amorphous powder. ESMS *m/z* 739.1845 $[M-1]^+$, $C_{43}H_{31}O_{12}$, calculated 739.1816; *m/z* 741.1960 $[M+1]^+$, $C_{43}H_{33}O_{12}$, calculated 741.1972. ^1H and ^{13}C NMR data are shown in Table 1.

3.3. Chamaechromone (*2*)

Brown amorphous powder. Low-resolution ESMS *m/z* 543.0 $[M+1]^+$; *m/z* 564.9 $[M+Na]^+$). The high-resolution ESMS *m/z* 199.0753 ($C_{13}H_{11}O_2$) and *m/z* 344.0531 ($C_{17}H_{12}O_8$). ^1H and ^{13}C NMR data are shown in Table 1.

3.4. (−)-Epiafzelechin 7-O-β-D-glucopyranoside (*3*)

Amorphous powder. Low-resolution POSFAB *m/z* 436.3. ^1H and ^{13}C NMR (500 MHz, CD_3OD–D_2O (2:1)): δ 2.53 (1H, dd, $J = 16.48$, 8.45 Hz, H_a-4), 2.89 (1H, dd, $J = 16.48$, 5.50 Hz, H_b-4), 3.40 (4H, m, H-2″, 3″, 4″, 5″), 3.68 (1H, dd, $J = 12.00$, 4.50 Hz, H_a-6″), 3.87 (1H, dd, $J = 12.00$, 1.05 Hz, H_b-6″), 4.00 (1H, ddd, $J = 8.45$, 7.65, 5.50 Hz, H-3), 4.60 (1H, d, $J = 7.65$ Hz, H-2), 4.81 (1H, d, $J = 7.50$ Hz, H-1″), 6.14 (1H, d, $J = 2.24$ Hz, H-6), 6.20 (1H, d, $J = 2.24$ Hz, H-8), 6.78 (2H, d, $J = 8.38$ Hz, H-3′, 5′), 7.20 (2H, d, $J = 8.38$ Hz, H-2′, 6′); δ 28.86 (C-4), 62.46 (C-6″), 68.59 (C-3), 71.31 (C-4″), 74.82 (C-3″), 77.99 (C-2″, 5″), 82.91 (C-2), 96.88 (C-6), 97.43 (C-8), 102.17 (C-1″), 103.69 (C-10), 116.05 (C-3′, 5′), 129.60 (C-2′, 6′), 131.30 (C-1′), 156.88 (C-5), 157.45 (C-9), 158.37 (C-4′), 158.57 (C-7).

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References

Dhaon, R., Jian, G. K., Sarin, J. P. S., & Khanna, N. M. (1989). *Indian J. Chem. B, 28B,* 982.

Niwa, M., Liu, Q., Tatematsu, H., & Hirata, Y. (1984). *Tetrahedron Letters, 25,* 3735.