

Two New Glucosides from Radix *Polygoni multiflori* Preparata

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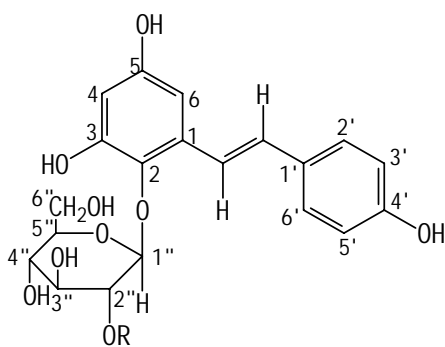
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Abstract: 2,3,5,4'-tetrahydroxystilbene-2-O-(2''-O-feruloyl)- β -D-glucopyranoside, 2,3,5,4'-tetrahydroxystilbene-2-O-(2''-O-*p*-coumaroyl)- β -D-glucopyranoside were isolated from Radix *Polygoni multiflori* Preparata. Structures were elucidated by chemical and spectral evidences.

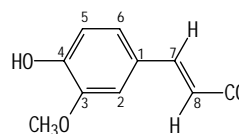
Keywords: Radix *Polygoni multiflori* Preparata, 2,3,5,4'-tetrahydroxystilbene-2-O-(2''-O-feruloyl)- β -D-glucopyranoside, 2,3,5,4'-tetrahydroxystilbene-2-O-(2''-O-*p*-coumaroyl)- β -D-glucopyranoside.

The root tuber of *Polygonum multiflorum* Thunb. (Polygonaceae) (PM) is a famous Chinese traditional medicine, which has been used to remedy for treatment many diseases such as cardiovascular and aging diseases for long times. When it is used as a tonic drug, PM must be prepared in order to eliminate its side effects, and the preparation is known as *Radix Polygoni multiflori* Preparata (PMP)¹. Here we report the isolation of 2,3,5,4'-tetrahydroxystilbene-2-O-(2''-O-feruloyl)- β -D-glucopyranoside (1), 2,3,5,4'-tetrahydroxystilbene-2-O-(2''-O-*p*-coumaroyl)- β -D-glucopyranoside (2) from the butanol-soluble fraction of PMP, and structural elucidation of these two new glucosides (scheme).

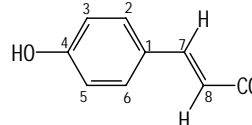
Scheme



1 R=feruloyl



2 R=*p*-coumaroyl



The 80% EtOH extract of PMP was partitioned with petroleum ether, chloroform and *n*-butanol, respectively. The *n*-BuOH fraction was further fractionated by non-polar macroreticular resin DA-201, silica gel, sephadex LH-20 and ODS RP-18 column chromatography to afford **1** and **2**.

Compound **1**, pale brown needles (MeOH), mp 202 ~ 203°C, FAB-MS *m/z*: 582 (M^+), EI-MS *m/z*: 244 (M^+ -glc). According to the data of the $^1\text{H-NMR}$ and DEPT spectra, the molecular formula was deduced to be $\text{C}_{30}\text{H}_{30}\text{O}_{12}$. The $^1\text{H-}$ and $^{13}\text{C-NMR}$: spectra data of **1** are listed in **Table1**.

Table 1 The $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra data of **1** (DMSO- d_6)

H	δ ppm	J_{Hz}	C	δ ppm
Stilbene-4	6.22(d)	2.7	Stilbene-1	132.0s
6	6.48(d)	2.7	2	134.5s
2',6'	7.38(m)		3	150.1s
3',5'	6.78(m)		4	102.9d
α	7.21(d)	16.4	5	154.1s
β	6.88(d)	16.4	6	101.4d
Feruloyl- 2	7.20(d)	1.8	1'	128.9s
5	7.42(d)	8.3	2',6'	127.9d
6	7.01(dd)	8.3, 1.8	3',5'	116.3d
7	7.60(d)	15.2	4'	157.3s
8	6.46(d)	15.2	α	120.0d
OCH ₃	3.70(s)		β	128.7d
β -glucosyl-1"	4.92(d)	8.0	Feruloyl-1	125.6s
2"	5.06(dd)	8.0, 8.0	2	111.3d
3"	3.58(m)		3	147.8s
4"	3.40(m)		4	149.2s
5"	3.22(m)		5	115.5d
6"	3.60(m)		6	122.7d
			7	145.2d
			8	114.5d
			COO	165.9s
			OCH ₃	55.6q
			β -glucosyl-1"	101.7d
			2"	74.0d
			3"	74.0d
			4"	69.7d
			5"	77.0d
			6"	60.6t

The $^1\text{H-NMR}$ spectrum suggested the presence of two double bonds each in *E* configuration according to the coupling constant of signals at δ 6.88 (1H, d, $J = 16.4\text{Hz}$), 7.21 (d, 1H, $J = 16.4\text{Hz}$), 6.46 (d, 1H, $J = 15.2\text{Hz}$), 7.60 (d, 1H, $J = 15.2\text{Hz}$), a benzene moieties which was substituted by three groups in 1,2,4 position respectively [δ 7.00 (dd, 1H, $J = 8.3, 1.8\text{Hz}$), 7.20 (d, 1H, $J = 1.8\text{Hz}$) and 7.42 (d, 1H, $J = 8.3\text{Hz}$)], another pair of *meta*-aromatic protons [δ 6.22 (d, 1H, $J = 2.7\text{Hz}$), 6.48 (d, 1H, $J = 2.7\text{Hz}$)], a *para*-substituted benzene moieties [δ 6.78 (m, 2H), δ 7.38(m, 2H)], four aromatic hydroxyl (δ 8.6, 9.1, 9.6, 9.7) and a methoxyl [δ 3.70 (s, 3H)]. $^{13}\text{C-NMR}$ and DEPT spectra indicated the presence of a carbonyl group (δ 165.9), a *para*-substituted benzene

(four aromatic carbon: δ 116.3, δ 127.9). All the evidence above demonstrated that there were three benzenes and two *trans*-double bonds. Compared with NMR spectra of 2,3,5,4'-tetrahydroxystilbene-2-O- β -D-glucopyranoside², it was found easily that **1** was composed of 2,3,5,4'-tetrahydroxystilbene-2-O- β -D-glucopyranoside and another moieties, including a carbonyl, a benzene, a *trans*-double bond, a hydroxyl and a methoxy group.

In order to confirm the ascription of all NMR signals and the location of every substituent, the HMQC, HMBC and NOESY were introduced. In HMBC spectrum, the correlation among δ_C 165.9 and δ_H 6.46, 7.60 revealed the presence of -CH = CH-COO group. The fact that correlation between δ_H 7.2 and δ_C 149.2 was observed in HMBC spectrum, as well as the fact that correlation between δ_H 7.2 and δ_H 3.70 was also observed in NOESY spectrum, suggested the presence of 3-methoxy, 2-aromatic proton. All the facts above indicated the presence of feruloyl group.

Six signals ranging from δ 62.3 to δ 104.9 in DEPT spectrum suggested the presence of a glucosyl group. The signal of anomeric proton (δ 4.92, d, J = 8.0Hz) revealed that this glucose should be β -D-glucose, which was also supported by the HCl hydrolysis of **1**. According to the fact that δ_H 5.06 (dd, 1H, J = 8.0, 8.0Hz) was correlative with δ_C 74.0 (HMQC) and δ_H 4.92 (¹H-¹HCOSY), it could be concluded that the C-2 hydroxyl group in glucose moiety must be substituted by a group with strong shielding activity. The correlation between δ_H 5.06 and δ_C 165.9 in HMBC indicated that the feruloyl was connected to the C-2 hydroxyl group in glucose moiety.

From these chemical and spectral evidences, **1** is identified as 2,3,5,4'-tetrahydroxystilbene-2-O-(2''-O-feruloyl)- β -D-glucopyranoside.

The compound **2** was a colorless needles (crystallized from MeOH), mp 197~198°C, FAB-MS *m/z*: 552 (M⁺), EI-MS *m/z*: 244 (M⁺-glc). According to the data of the ¹H-NMR and DEPT spectra, the molecular formula was deduced to be C₂₉H₂₈O₁₁. The ¹H- and ¹³C-NMR spectra data of **2** are listed in **Table 2**.

The ¹³C-NMR as well as DEPT spectrum revealed the similar signals to those of **1** except lacking of a methoxyl signal. Thus, the feruloyl of **1** might be replaced by a coumaroyl. The spectra of ¹H- and ¹³C-NMR exhibited typical signals of *p*-coumaroyl group³.

Refer to all NMR signals of **1**, together with the techniques of HMQC, HMBC, NOESY, the ascription of all NMR signals and the location of every substituent of **2** were confirmed.

From these chemical and spectral evidences, **2** was assigned as 2,3,5,4'-tetrahydroxystilbene-2-O-(2''-O-*p*-coumaroyl)- β -D-glucopyranoside.

Table 2 The ^1H - and ^{13}C -NMR spectra data of **2** (CD_3OD)

H	δ ppm	J_{Hz}	C	δ ppm
Stilbene-4	6.23(d)	2.9	Stilbene-1	133.1s
6	6.55(d)	2.9	2	136.5s
2',6'	7.39(m)		3	152.0s
3',5'	6.74(m)		4	103.9d
α	7.18(d)	16.3	5	155.9s
β	6.93(d)	16.3	6	103.4d
coumaroyl- 2,6	7.19(m)		1'	131.7s
3,5	6.74(m)		2',6'	129.4d
7	7.58(d)	15.8	3',5'	116.6d
8	6.32(d)	15.8	4'	158.7s
β -glucosyl-1"	4.93(d)	8.2	α	120.9d
2"	5.19(dd)	8.2, 8.1	β	130.9d
3"	3.67(m)		coumaroyl-1	127.1s
4"	3.60(m)		2,6	131.3d
5"	3.35(m)		3,5	116.8d
6"	3.80(m)		4	161.3s
			7	147.5d
			8	114.9d
			COO	168.6s
			β -glucosyl-1"	104.6d
			2"	75.3d
			3"	76.1d
			4"	71.1d
			5"	78.5d
			6"	62.0t

Acknowledgments

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