PERGAMON

Phytochemistry 50 (1999) 677–680

PHYTOCHEMISTRY

Phenylpropanoid glycosides from *Stellera chamaejasme*

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Received 4 March 1998; accepted 27 July 1998

Abstract

Two new phenylpropanoid glycosides, [4-(3-β-D-glucopyranosyloxy-1-*E*-propenyl)-2,6-dimethoxyphenyl]-6-*O*-β-D-glucopyranosyl-β-D-glucopyranoside and [4-(3-hydroxy-1-*Z*-propenyl)-2,6-dimethoxyphenyl]-6-*O*-β-D-glucopyranosyl-β-D-glucopyranoside were isolated from the root of *Stellera chamaejasme* along with four known phenylpropanoid glycosides, coniferinoside, syringin, syringinoside, sinapyl alcohol 1,3-diglucopyranoside. Their structures were established on the basis of spectral and chemical evidence.

Keywords: *Stellera chamaejasme*; Thymelaeaceae; Root; Phenylpropanoid; Glycoside

1. Introduction

From the water soluble fraction of the root of *Stellera chamaejasme* L. (Thymelaeaceae) six phenylpropanoid glycosides were isolated by chromatographic methods. [4-(3-β-D-glucopyranosyloxy-1-*E*-propenyl)-2,6-dimethoxyphenyl]-6-*O*-β-D-glucopyranosyl-β-D-glucopyranoside (**1**) and [4-(3-hydroxy-1-*Z*-propenyl)-2,6-dimethoxyphenyl]-6-*O*-β-D-glucopyranosyl-β-D-glucopyranoside (**2**) are new compounds. Compound **1** is the 9-glycoside of syringinoside while compound **2** is the *cis*-isomer of syringinoside (**4**). The structures were elucidated mainly by two-dimensional NMR spectroscopy. Coniferinoside (**3**), syringinoside (**4**), syringin (**5**) and sinapyl alcohol 1,3-di-*O*-β-D-glucopyranoside (**6**) are reported for the first time from this plant.

2. Results and discussion

Dried roots of *Stellera chamaejasme* were extracted with 80% ethanol and dried. The dry extract was suspended in water and extracted with ether and *n*-BuOH. The *n*-BuOH fraction (20 g) was applied to a Sephadex G15 column followed by semi-preparative HPLC C-18 to provide compound 1 and 2 (3.5 mg and 2 mg) along with compounds **3**, **4**, **5** and **6**.

Compounds **3**, **4**, **5**, **6** were identified as coniferinoside, syringinoside, syringin and sinapyl alcohol 1,9-di-*O*-β-D-glucopyranoside, by comparison with the authentic NMR spectroscopic data reported in the literature (Niwa, Iwadare, Wu & Hirata, 1988; Ono, Ito, Ishikawa, Katajima, Tanaka et al., 1996; Sugiyama, Nagayama & Kikuchi, 1993). The assignment of ^{13}C signals of **4** was based on its HMQC and HMBC experiments.

Compound 1 was isolated as an amorphous powder. $[\alpha]_D^{20}$ −50.6 (MeOH). The ESMS of 1 showed *m*/*z* 719.0 $[M + Na]^+$. The UV spectrum showed absorption maxima at 220 nm and 266 nm. The ^1H NMR spectrum indicated the presence of a pair of aromatic protons (δ 6.77, *s*), methylene protons [δ 4.30 (*dd*, $J = 12.5$, 7.0 Hz, H_a-9) and δ 5.00 (*dd*, $J = 12.5$, 6.0 Hz, H_b-9)], two olefinic protons [δ 6.28 (*ddd*, $J = 16.0$, 7.0, 6.0 Hz, H-8) and δ 6.57 (*d*, $J = 16.0$ Hz, H-7)] in pre *trans*-configurations, and two methoxy groups [δ 3.77(*s*)], suggesting the presence of a phenylpropanoid moiety, and three signals at δ 4.17 (*d*, $J = 7.5$ Hz), δ 4.45 (*d*, $J = 7.8$ Hz) and δ 5.00 (*d*, $J = 7.6$ Hz) assignable to three anomeric protons of sugars. The ^{13}C NMR spectrum confirmed the presence of a phenylpropanoid moiety. The ^{13}C signal pattern and the coupling constant ($J = 7.5$–7.8 Hz) of the anomeric proton of the sugar showed that **1**

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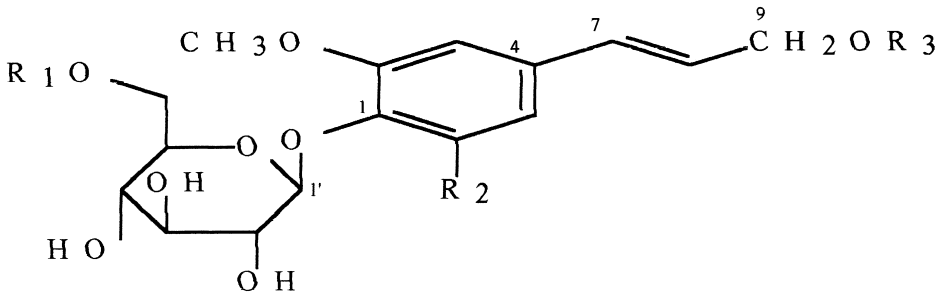
0031-9422/98 $ - see front matter
PII: S0031-9422(98)00586-X



1 R_1=β-D-Glc(carbon atoms numbered 1''~6''), R_2= OCH_3, R_3=β-D-Glc(carbon atoms numbered 1'''~6''')

2 *cis*-isomer of **4**

3 R_1=β-D-Glc(carbon atoms numbered 1''~6''), R_2=H, R_3=H

4 R_1=β-D-Glc(carbon atoms numbered 1''~6''), R_2=OCH_3, R_3=H

5 R_1=H, R_2=OCH_3, R_3=H

6 R_1=H, R_2=OCH_3, R_3=β-D-Glc(carbon atoms numbered 1''~6'')

contained three β-D-glucose molecules. The position of the glucosyl linkage in **1** was investigated by HMBC NMR spectroscopy. The long-range coupling between H-1 (δ 4.45, 1H, *d*, J = 7.8 Hz) and C-9 (δ 70.75) suggested there was a glucose attached to C-9. The long-range coupling between H-1 and C-6 revealed the existence of a gentiobiose unit. Although the long-range coupling of H-1 and C-1 was not observed, since the glucosyl moiety had been assigned to C-9 there was only one possibility for the gentiobiose unit attach to the phenylpropanoid moiety, which is C-1 to OH-1. This linkage was confirmed by comparison with the NMR data of compound **6**. β-Glucosidase hydrolysis of **1** followed by TLC [Silica gel, *n*-BuOH-acetone-H_2O (4:5:1)] showed that the hydrolysate consists of D-glucose and gentiobiose. On the basis of the above data, **1** was elucidated to be [4-(3-β-D-glucopyranosyloxy-1-*E*-propenyl)-2,6-dimethoxyphenyl]-6-*O*-β-D-glucopyranosyl-β-D-glucopyranoside.

Compound **2** was isolated as an amorphous powder. $[\alpha]_D^{20}$ −33.7 (MeOH). Its ESMS showed *m/z* 557.0 $[M + Na]^+$. The UV spectrum showed absorption maxima at 218 nm and 259 nm. The ^1H and ^{13}C NMR signals of **2** were similar to compound **4**, except for the signals of the propenyl portion. The smaller coupling constant between H-7 and H-8, J = 11.8 Hz, and the upfield shift of C-9 of **2** suggested that the olefinic protons had a *cis*-configuration. The linkage between the sugar and the phenylpropanoid moiety was confirmed by the HMBC NMR spectroscopy. The long-range coupling of H-1 to C-6, and H-1 to C-1 suggested that a gentiobiose was attached to the phenylpropanoid moiety at C-1. β-glucosidase hydrolysis of **2** followed by TLC [Silica gel, *n*-BuOH-acetone-H_2O (4:5:1)] showed that the hydrolysate consists of D-glucose and gentiobiose. Thus, compound **2** was identified as [4-(3-hydroxy-1-*Z*-propenyl)-2,6-dimethoxyphenyl]-6-O-β-D-glucopyranosyl-β-D-glucopyranoside.

3. Experimental

^1H and ^{13}C NMR spectra were recorded on a Varian NMR Unity 300 MHz, while HMQC and HMBC NMR spectra were recorded on a Varian NMR Unity 500 MHz. Chemical shifts are given in δ (ppm). Mass spectra were recorded on a Micromass Zabspec Oatof spectrometer.

3.0.1. Extraction and isolation

Dried root of *S. chamaejasme* L. (1 kg) collected on June 7, 1993, in Daqing, China, was extracted with

Table 1
^{13}C and ^{1}H NMR spectral data for compounds **1** and **2** (300 MHz, D_2O; δ in ppm)

	Compound 1		Compound 2	
Position	^{13}C	^{1}H	^{13}C	^{1}H
1	134.56		134.50	
2	153.30		152.93	
2–OMe, 6–OMe	56.95	3.77, 6H, *s*	57.00	3.79, 6H, *s*
3	105.16	6.77, 1H, *s*	107.50	6.60, 1H, *s*
4	133.57		134.50	
5	105.16	6.77, 1H, *s*	107.50	6.60, 1H, *s*
6	153.30		153.93	
7	133.81	6.57, 1H, *d*, *J* = 16.0 Hz	131.35	6.54, 1H, *dt*, *J* = 11.80, 1.50 Hz
8	125.98	6.28, 1H, *ddd*, *J* = 16.0, 7.0, 6.0 Hz	131.35	5.81, 1H, *dt*, *J* = 11.80, 6.65 Hz
9	70.75	4.30, 1H, *dd*, *J* = 12.5, 7.0 Hz4.42, 1H, *dd* (partly overlapped), *J* = 12.5, 6.0 Hz	59.03	4.33, 2H, *ddd*, *J* = 6.65, 1.50, 1.50 Hz
1	102.79	5.00, 1H, *d*, *J* = 7.6 Hz	102.93	5.04, 1H, *d*, *J* = 7.45 Hz
2′,3′,4′,5′		Proton signals are overlapped		Proton signals are overlapped
6′	68.08	3.74, 1H, *dd* (overlapped)3.93, 1H, *dd*, *J* = 12.0, 1.0 Hz	68.19	3.80, 1H, (*dd*, overlapped)3.98, 1H, *dd*, *J* = 12.50, 1.50 Hz
1″	102.73	4.17, 1H, *d*, *J* = 7.5 Hz	102.79	4.43, 1H, *d*, *J* = 7.58 Hz
2″,3″,4″,5″		Proton signals are overlapped		Proton signals are overlapped
6″	61.48	3.61, 1H, *dd*, *J* = 12.5, 6.0 Hz3.93, 1H, *dd*, *J* = 12.5, 2.0 Hz	61.43	3.59, 1H, *dd*, *J* = 12.00, 6.00 Hz3.79, 1H (*dd*, overlapped)
1‴	101.75	4.45, 1H, *d*, *J* = 7.8 Hz		
2‴,3‴,4‴,5‴		Proton signals are overlapped		
6‴	61.40	3.54, 1H, *dd*, *J* = 12.5, 6.0 Hz 3.76, 1H, *dd* (overlapped)		
2′–5′,2″–5″ and 2‴–5‴		carbon signals at 70.06, 70.23, 70.37, 73.70, 73.83, 74.23, 76.26, 76.43, 76.50(2C), 76.60, 77.06	2′–5′ and 2″–5″	carbon signals at 70.07, 70.24, 73.73, 74.00, 74.25, 76.42, 76.56, 76.97

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. The *n*-BuOH fraction (ca. 20 g) was chromatographed on a Sephadex G15 column (60×400 mm), eluted with MeOH–H_2O 1:3 to 2:1 gradient, and then loaded into a Supelcosil LC-18 (10×250 mm) column with UV detector at 254 nm on Waters LC Module I HPLC, 5% to 30% MeCN–H_2O gradient, 4 ml/min, to obtain 1 (3.5 mg), 2 (2.0 mg), 3 (13.3 mg), 4 (126.5 mg), 5 (12.3 mg) and 6 (7.6 mg), with compounds 3–6 being identified as described in Niwa et al., 1988; Ono et al., 1996; Sugiyama et al., 1993.

*3.0.2. Enzymatic hydrolysis of [4-(3-β-D-glucopyranosyloxy-1-E-propenyl)-2,6-dimethoxyphenyl]-6-O-β-D-glucopyranosyl-β-D-glucopyranoside(**1**) and [4-(3-hydroxy-1-Z-propenyl)-2,6-dimethoxyphenyl]-6-O-β-D-glucopyranosyl-β-D-glucopyranoside(**2**)*

Approximately 0.1 mg of compound **1** and **2** were dissolved in 3 drops of water and to each was added a small amount of β-glucosidase from almonds (Fluca), The solutions were kept at 37°. The hydrolysate were checked with Silica gel TLC[Aldrich Z12,274-2, *n*-BuOH-acetone-H_2O (4:5:1)] at 24 and 48 hrs, D-glucose and gentibiose (Fluca) as references. The spots on TLC were visualized by spraying with aniline–diphenylamine reagent(aniline sulfate 2.7% w/v, diphenylamine 1.8% w/v, in acetone with H_2SO_4 2% v/v) and heated at 110°. The rf values of the hydrolysates, in both cases, were identical with those of D-glucose and β-gentiobiose.

*3.0.3. [4-(3-β-D-Glucopyranosyloxy-1-E-propenyl)-2,6-dimethoxyphenyl]-6-O-β-D-glucopyranosyl-β-D-glucopyranoside(**1**)*

Amorphous powder. $[\alpha]_D^{20}$ −50.6 (MeOH, *c* = 0.190). ESMS *m/z* 719.0 $[M + Na]^+$. UV λ_{max}^{MeOH} = 220nm, 266 nm. ^{1}H and ^{13}C NMR data are shown in Table 1.

*3.0.4. [4-(3-Hydroxy-1-Z-propenyl)-2,6-dimethoxyphenyl]-6-O-β-D-glucopyranosyl-β-D-glucopyranoside(**2**)*

Amorphous powder. $[\alpha]_D^{20}$ −33.7 (MeOH, *c* = 0.234). ESMS *m/z* 557.0 $[M + Na]^+$. UV λ_{max}^{MeOH} = 281 nm, 259 nm. ^{1}H and ^{13}C NMR data are shown in Table 1.

Acknowledgements

The authors wish to thank Dr. T. Nakashima for performing 500 MHz NMR. This research is partially funded by SynPhar Laboratories Inc. of Edmonton.

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