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Phenylpropanoid glycosides from *Smilax glabra*

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Abstract

Five phenylpropanoid esters of sucrose glycosides, trivially named smiglasides A–E, were isolated from the rhizomes of *Smilax glabra*. Their structures were elucidated on the basis of spectroscopic studies.

Keywords: *Smilax glabra*; Liliaceae; Phenylpropanoid glycosides; Sucrose ester; Smiglaside

1. Introduction

The rhizome of *Smilax glabra* (Liliaceae) has been used extensively in traditional chinese medicine to treat syphilis, acute bacterial dysentery, acute and chronic nephritis, and other conditions (Chinese Materia Medica Dictionary, 1977). However, only a few papers have described its constituents (Yi, Cao, Yang, Hong, Cao & Leng, 1995; Li, Yi, Tang & Xiao, 1996; Chen, Shen & Jian, 1996). In our previous paper, we reported the isolation and structural elucidation of a new compound named smitilbin, and seven known compounds from fraction 1 or 2 obtained from the rhizome of *S. glabra*, and their structural requirements for preventing immunological hepatocyte damage (Chen, Li, Cao, Xu, Komatsu & Namba, 1999). Further phytochemical studies on fraction 3 have led to the isolation of five phenylpropanoid glycosides, each having a sucrose core, together with two other known compounds. In this paper, we report the isolation and structure elucidation of these compounds by the use of 2D-NMR spectral techniques.

2. Results and discussion

Compounds **1**–**5** were isolated from the dried rhizome of *S. glabra*, together with the previously described closely related analogue helonioside A (**6**) (Nakano, Murakami, Takaishi & Tomimatsu, 1986) and (3,6-di-*O*-feruloyl)-β-D-fructofuranosyl-(3,6-di-*O*-acetyl)-α-D-glucopyranoside (**7**) (Miyase & Ueno, 1993). Smiglaside A (**1**), an amorphous powder, showed $[\alpha]_D$ 79.53° (MeOH) and its molecular formula was determined as $C_{48}H_{52}O_{23}$ by high-resolution FAB mass spectrometry. The UV spectrum showed absorptions at 216 and 328 nm, and in the IR, spectral absorptions attributable to hydroxyl (3425 cm^{-1}) and ester groups were observed (1740, 1720 and 1710 cm^{-1}). The ^{1}H-NMR spectrum of **1**, extensively analyzed with the aid of ^{1}H–^{1}H COSY, indicated signals due to three *trans*-double bonds, three 1,3,4-trisubsti-

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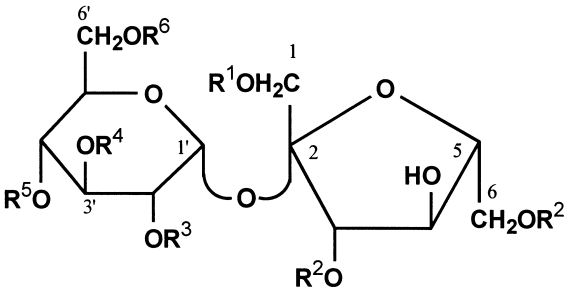
tuted phenyl groups, three methoxyl groups, three acetyl groups, eight oxymethines and three oxymethylenes (Table 1). The ^{13}C-NMR spectrum showed 12 oxygen-bearing carbon signals including two anomers (Table 2). These data suggested that **1** should be a phenylpropanoid glycoside including three cinnamic acid residues and two sugars (Shimomura, Sashida & Mimaki, 1986). Detailed analysis of ^{1}H and ^{13}C-NMR spectral data of **1** with the aid of DEPT, ^{1}H–^{1}H COSY, HMQC and HMBC indicated that the two sugars were a disaccharide, sucrose, containing α-D-glucose and β-D-fructose moieties (Shimomura et al., 1986; Kashiwada, Nonaka & Nishioka, 1988).

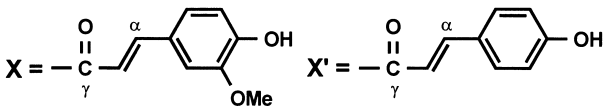
An HMBC experiment (8.9 μs delay; similar throughout) was conducted in order to determine ^{13}C–^{1}H connectivities. The clear long-range correlations, C4‴/H-2‴, 6‴, and C4″, 4⁗/H-2″, 6″, 2⁗, 6⁗ in the HMBC spectrum indicated that the ester groups were feruloyl, even though C4″ and C-4⁗ carbons resonated at δ 150.62 and 150.66, and were indistinguishable. Likewise, the other long-range correlations [C═O (C-γ″, δ 168.14)/H_2-1, C═O (C-γ‴, δ 167.82)/H-3 and C═O (C-γ⁗, δ 168.66)/H_2-6] provided clues for joining three feruloyl groups at the C-1, C-3 and C-6 positions of fructose. Moreover, the long-range correlations [C═O (δ 172.11)/H-2′, C═O (δ 171.59)/H-4′ and C═O (δ 172.43)/H-6′] enabled us to assign three acetyl groups to C-2′, C-4′ and C-6′ of glucose.

Table 1
^{1}H-NMR spectral data of simiglasides A (**1**), B (**2**), C (**3**), D (**4**) and E (**5**) (δ value in CD_3OD and coupling constants in Hz. *Signal pattern unclear due to overlapping. Signals bearing the same alphabatical superscript in each column may be interchanged.)

H	1	2	3	4	5
β-D-fructose					
1	4.39 (*d*, *J* = 11.5)	4.31 (*d*, *J* = 11.5)	3.71 (*d*, *J* = 12.0)	4.39 (*d*, *J* = 11.6)	4.29 (*d*, *J* = 11.6)
2	4.23 (*d*, *J* = 11.5)	4.21 (*d*, *J* = 11.5)	3.47 (*d*, *J* = 12.0)	4.23 (*d*, *J* = 11.6)	4.18 (*d*, *J* = 11.6)
3	5.47 (*d*, *J* = 7.7)	5.54 (*d*, *J* = 8.2)	5.49 (*d*, *J* = 7.9)	5.49 (*d*, *J* = 7.5)	5.54 (*d*, *J* = 8.2)
4	4.45 (*t*, *J* = 7.7)	4.46 (*t*, *J* = 8.2)	4.47 (*t*, *J* = 7.9)	4.47 (*t*, *J* = 7.5)	4.44 (*t*, *J* = 8.2)
5	4.18 (*m*)	4.19*	4.14 (*m*)	4.17 (*td*, *J* = 7.5, 3.6)	4.17*
6	4.52 (*dd*, *J* = 12.0, 3.4)	4.51 (*dd*, *J* = 12.0, 3.6)	4.54 (*dd*, *J* = 12.0, 2.6)	4.51 (*dd*, *J* = 12.0, 3.6)	4.51 (*m*)
	4.44 (*dd*, *J* = 12.0, 7.0)	4.45 (*m*)	4.48 (*dd*, *J* = 12.0, 5.6)	4.43 (*dd*, *J* = 12.0, 7.5)	4.46 (*m*)
α-D-glucose					
1′	5.75 (*d*, *J* = 3.8)	5.67 (*d*, *J* = 3.8)	5.72 (*d*, *J* = 3.8)	5.47 (*d*, *J* = 3.7)	5.68 (*d*, *J* = 3.4)
2′	4.71 (*dd*, *J* = 10.0, 3.8)	4.64 (*dd*, *J* = 10.0, 3.8)	4.66 (*dd*, *J* = 9.9, 3.8)	4,70 (*dd*, *J* = 10.0, 3.7)	4.64 (*dd*, *J* = 9.8, 3.4)
3′	3.96 (*t*, *J* = 10.0)	3.86 (*t*, *J* = 10.0)	3.90 (*t*, *J* = 9.9)	3.96 (*t*, *J* = 10.0)	3.84 (*t*, *J* = 9.8)
4′	4.83 (*t*, *J* = 10.0)	3.35 (*t*, *J* = 10.0)	4.80 (*t*, *J* = 9.9)	4.83 (*t*, *J* = 10.0)	3.34 (*t*, *J* = 9.8)
5′	4.26 (*ddd*, *J* = 10.0, 6.0, 2.0)	4.17*	4.26 (*ddd*, *J* = 9.9, 5.3, 2.2)	4.28 (*ddd*, *J* = 10.0, 5.8, 2.1)	4.15*
6′	4.21 (*dd*, *J* = 12.0,2.0)	4.54 (*dd*, *J* = 12.0, 2.0)	4.23 (*dd*, *J* = 12.0, 2.2)	4.20 (*dd*, *J* = 12.0, 2.1)	4.53 (*dd*, *J* = 12.0, 2.0)
	4.09 (*dd*, *J* = 12.0, 6.0)	4.16*	4.10 (*dd*, *J* = 12.0, 5.3)	4.09 (*dd*, *J* = 12.0, 5.8)	4.18*
2′-OAc	2.11 (*s*)	2.10 (*s*)	2.08 (*s*)	2.10 (*s*)	2.10 (*s*)
4′-OAc	1.88 (*s*)	–	1.85 (*s*)	1.88 (*s*)	–
6′OAc	2.04 (*s*)	2.08 (*s*)	2.03 (*s*)	2.03 (*s*)	2.08 (*s*)
1 − *X* or *X*′					
α″	7.66 (*d*, *J* = 16.0)[a]	7.64 (*d*, *J* = 16.0)	–	7.66 (*d*, *J* = 16.0)[a]	7.65 (*d*, *J* = 16.0)
β″	6.38 (*d*, *J* = 16.0)	6.37 (*d*, *J* = 16.0)	–	6.35 (*d*, *J* = 16.0)	6.34 (*d*, *J* = 16.0)
2″	7.16 (*d*, *J* = 2.0)	7.15 (*d*, *J* = 1.8)	–	7.43 (*d*, *J* = 8.5)	7.42 (*d*, *J* = 8.7)
3″	–	–	–	6.75 (*d*, *J* = 8.5)	6.74 (*d*, *J* = 8.7)
5″	6.76 (*d*, *J* = 8.2)	6.75 (*d*, *J* = 8.2)	–	6.75 (*d*, *J* = 8.5)	6.74 (*d*, *J* = 8.7)
6″	7.04 (*dd*, *J* = 8.2, 2.0)	7.04 (*dd*, *J* = 8.2, 1.8)	–	7.43 (*d*, *J* = 8.5)	7.42 (*d*, *J* = 8.7)
OMe	3.88[b]	3.88[a]	–	–	–
3 − *X*					
α‴	7.70 (*d*, *J* = 16.0)	7.70 (*d*, *J* = 16.0)	7.70 (*d*, *J* = 16.0)	7.72 (*d*, *J* = 16.0)	7.72 (*d*, *J* = 16.0)
β‴	6.45 (*d*, *J* = 16.0)	6.48 (*d*, *J* = 16.0)	6.44 (*d*, *J* = 16.0)	6.47 (*d*, *J* = 16.0)	6.49 (*d*, *J* = 16.0)
2‴	7.23 (*d*, *J* = 2.0)	7.28 (*d*, *J* = 1.8)	7.26 (*d*, *J* = 1.8)	7.25 (*d*, *J* = 2.0)	7.25 (*d*, *J* = 1.8)
5‴	6.81 (*d*, *J* = 8.0)	6.81 (*d*, *J* = 8.2)	6.83 (*d*, *J* = 8.2)	6.83 (*d*, *J* = 8.0)	6.82 (*d*, *J* = 8.2)
6‴	7.10 (*dd*, *J* = 8.0, 2.0)	7.13 (*dd*, *J* = 8.2, 1.8)	7.12 (*dd*, *J* = 8.2, 1.8)	7.12 (*dd*, *J* = 8.0, 2.0)	7.11 (*dd*, *J* = 8.2, 1.8)
OMe	3.89[b]	3.89[a]	3.91 (*s*)	3.90[b]	3.90[a]
6 − *X*					
α⁗	7.65 (*d*, *J* = 16.0)[a]	7.64 (*d*, *J* = 16.0)	7.67 (*d*, *J* = 16.0)	7.67 (*d*, *J* = 16.0)[a]	7.65 (*d*, *J* = 16.0)
β⁗	6.40 (*d*, *J* = 16.0)	6.40 (*d*, *J* = 16.0)	6.41 (*d*, *J* = 16.0)	6.42 (*d*, *J* = 16.0)	6.41 (*d*, *J* = 16.0)
2⁗	7.18 (*d*, *J* = 2.0)	7.18 (*d*, *J* = 1.8)	7.20 (*d*, *J* = 1.8)	7.20 (*d*, *J* = 2.0)	7.20 (*d*, *J* = 1.8)
5⁗	6.80 (*d*, *J* = 8.2)	6.80 (*d*, *J* = 8.0)	6.83 (*d*, *J* = 8.2)	6.80 (*d*, *J* = 8.0)	6.80 (*d*, *J* = 8.2)
6⁗	7.07 (*dd*, *J* = 8.2, 2.0)	7.08 (*dd*, *J* = 8.0, 1.8)	7.10 (*dd*, *J* = 8.2, 1.8)	7.08 (*dd*, *J* = 8.0, 2.0)	7.08 (*dd*, *J* = 8.2, 1.8)
OMe	3.84[b]	3.82[a]	3.91 (*s*)	3.89[b]	3.88[a]



	R^1	R^2	R^3	R^4	R^5	R^6
1:	X	X	Ac	H	Ac	Ac
2:	X	X	Ac	H	H	Ac
3:	H	X	Ac	H	Ac	Ac
4:	X'	X	Ac	H	Ac	Ac
5:	X'	X	Ac	H	H	Ac
6:	H	X	H	H	H	H
7:	H	X	H	Ac	H	Ac



Based on the above findings, it was concluded that the structure of this compound is represented by **1**, named smiglaside A.

Smiglaside B (**2**) was obtained as an amorphous powder and showed $[\alpha]_D$ 36.65° (MeOH). The negative ion FABMS exhibited the *quasi*-molecular ion peak at *m/z*: 953 $[M - H]^-$ and its molecular formula was determined to be $C_{46}H_{50}O_{22}$ by high-resolution FAB mass spectrometry. The ^1H and ^{13}C-NMR spectra of **2**, analyzed with the aid of ^1H–^1H COSY, DEPT and HMQC, were similar to those of **1** except for the disappearance of one acetyl group. Further detailed comparison of the ^1H-NMR spectra of **2** and **1** revealed a marked upfield shift of the H-4′ signal of glucose (**2** δ_H 3.35; **1** δ_H 4.83), indicating that an acetyl group at the 4′ position of glucose in **1** was absent in **2**. This was further supported by HMBC. Thus, the structure of smiglaside B was determined as given in **2**.

Smiglaside C (**3**), an amorphous powder, exhibited $[\alpha]_D$ 32.86° (MeOH) and its mass spectral data suggested that **3** had only two feruloyl moieties, whose locations were concluded to be at C-3 and C-6 of fructose, based on analysis of ^1H–^1H COSY, HMQC and HMBC spectra. Therefore, the structure of smiglaside C was established as **3**.

Smiglaside D (**4**), an amorphous powder, $[\alpha]_D$ 67.14° (MeOH), was determined to have the molecular formula $C_{47}H_{50}O_{22}$ by high-resolution FAB mass spectrometry. The ^1H and ^{13}C-NMR spectral data of **4** were similar to those of **1** except for the absence of signals due to a methoxyl and a 1,3,4-trisubstituted phenyl group, and the presence of additional signals assignable to a 1,4-disubstituted phenyl group (δ_H 6.75, *d*, $J = 8.5$ Hz, 2H, δ_C 116.83; δ_H 7.43, *d*, $J = 8.5$ Hz, 2H, δ_C 133.82). These data suggested the presence of a *para*-coumaroyl moiety instead of the feruloyl moiety in **1**. Moreover, the HMBC spectrum of **4** displayed long-range correlations between C-1″ and H-2″, 3″, H-α″, H-β″, C-γ″ and H_2-1, H-β″ indicating that the *para*-coumaroyl moiety was attached to C-1 of fructose. Based on the above findings, the structure of smiglaside D was concluded to be **4**.

The ^1H and ^{13}C-NMR spectra of smiglaside E were almost identical with those of **4** except for the disappearance of acetyl group signals. In a similar manner as for compound **2**, the structure of smiglaside E was elucidated as **5**.

The identities of known compounds **6** and **7** were determined by MS and spectral data. This is the first example of the isolation of phenylpropanoid glycosides with a sucrose core from this plant.

3. Experimental

General procedures followed exactly those described in Chen et al. (1999). Plant material, Extraction and isolation followed exactly that of Chen et al. (1999). From that preparation, fr. 3 was chromatographed over silica gel CC eluted with a gradient of $CHCl_3$–MeOH to give fr. 3–1 (20 mg), fr. 3–2 (4.2 g) and fr. 3–3 (55 mg). A part of fr. 3–2 (1.1 g) was purified repeatedly by Cosmosil 75C_{18}-OPN column chromatography with MeOH–H_2O (1 : 1) and preparative TLC ($CHCl_3$–MeOH, 20 : 1) to give helonioside A (**6**) (25 mg), smiglaside A (**3**) (20 mg), (3,6-di-*O*-feruloyl)-β-D-fructofuranosyl-(3,6-di-*O*-acetyl)-α-D-glucopyranoside (**7**) (12 mg) and fr 3–2–1. Fr. 3–2–1 (195 mg) was further separated by silica gel CC and preparative TLC to provide smiglaside C (**1**) (12 mg), smiglaside E (**4**) (20 mg), smiglaside B (**2**) (32 mg) and smiglaside D (**5**) (11 mg).

Smiglaside A (**1**): amorphous powder, $[\alpha]_D$: 79.53° (MeOH; *c* 0.4), UV λ_{max} (MeOH) nm (log ε): 216 (4.52), 328 (4.68), IR ν_{max} (KBr) cm^{-1}: 3425, 1740, 1720, 1710, 1620, 1600, 1500, 1150, 1020 cm^{-1}, positive ion FABMS *m/z*: 1019 $[M + Na]^+$, HR-FABMS *m/z*: $[M + Na]^+$ 1019.2787 (Calcd. for $C_{48}H_{52}O_{23}Na$: 1019.2797), ^1H and ^{13}C-NMR spectral data: Tables 1 and 2.

Smiglaside B (**2**): light yellow amorphous powder, $[\alpha]_D$: 36.65° (MeOH; *c* 0.7), UV λ_{max} (MeOH) nm (log ε): 218 (4.20), 328 (4.35), IR ν_{max} (KBr) cm^{-1}: 3400, 1740, 1720, 1700, 1620, 1600, 1530, 1140, 1020 cm^{-1}, negative ion FABMS *m/z*: 953 $[M - H]^-$, HR-

Table 2
^{13}C-NMR spectral data of smiglasides A (**1**), B (**2**), C (**3**), D (**4**) and E (**5**) (δ value in CD_3OD. The multiplicities of each carbon signal were determined by the distortionless enhancement by polarization transfer (DEPT) method and are indicated as *s*, *d*, *t* and *q*. Signal bearing the same alphabatical superscript in each column may be interchanged.)

Carbon	**1**	**2**	**3**	**4**	**5**
β-D-Fructose					
1	66.66 (*t*)	65.50 (*t*)	65.37 (*t*)	66.79 (*t*)	66.52 (*t*)
2	103.59 (*s*)	103.59 (*s*)	105.50 (*s*)	104.03 (*s*)	103.58 (*s*)
3	79.85 (*d*)	79.45 (*d*)	78.87 (*d*)	79.97 (*d*)	79.44 (*d*)
4	73.97 (*d*)	73.90 (*d*)	73.58 (*d*)	74.05 (*d*)	73.89 (*d*)
5	81.43 (*d*)	81.15 (*d*)	81.34 (*d*)	81.59 (*d*)	81.18 (*d*)
6	64.69 (*t*)	65.29 (*t*)	64.44 (*t*)	64.70 (*t*)	65.24 (*t*)
α-D-Glucose					
1′	90.62 (*d*)	90.71 (*d*)	90.08 (*d*)	90.69 (*d*)	90.68 (*d*)
2′	73.90 (*d*)	74.28 (*d*)	73.99 (*d*)	74.02 (*d*)	74.29 (*d*)
3′	69.74 (*d*)	72.09 (*d*)	69.47 (*d*)	69.86 (*d*)	72.14 (*d*)
4′	72.18 (*d*)	71.85 (*d*)	72.27 (*d*)	73.61 (*d*)	71.86 (*d*)
5′	69.92 (*d*)	72.13 (*d*)	69.77 (*d*)	70.04 (*d*)	72.09 (*d*)
6′	63.98 (*t*)	65.24 (*t*)	64.06 (*t*)	64.08 (*t*)	65.24 (*t*)
2′-OAc	172.11 (*s*)	172.48 (*s*)	172.12 (*s*)	172.26 (*s*)	172.48 (*s*)
	21.02 (*q*)	21.10 (*q*)	20.92 (*q*)	21.01 (*q*)	21.07 (*q*)
4′-OAc	171.59 (*s*)	–	171.74 (*s*)	171.57 (*s*)	–
	20.63 (*q*)	–	20.67 (*q*)	20.64 (*q*)	–
6′-OAc	172.43 (*s*)	172.83 (*s*)	172.61 (*s*)	172.60 (*s*)	172.84 (*s*)
	20.78 (*q*)	20.87 (*q*)	20.83 (*q*)	20.79 (*q*)	20.87 (*q*)
$1-X$ or X'					
α″	148.19 (*d*)	147.18 (*d*)	–	147.28 (*d*)	147.21 (*d*)
β″	114.75 (*d*)	114.86 (*d*)	–	114.56 (*d*)	114.58 (*d*)
γ″	168.14 (*s*)	168.28 (*s*)	–	168.29 (*s*)	168.28 (*s*)
1″	127.59 (*s*)	127.75 (*s*)	–	127.05 (*s*)	127.02 (*s*)
2″	111.58 (*d*)	116.67 (*d*)	–	133.82 (*d*)	131.30 (*d*)
3″	149.28 (*s*)[a]	149.32 (*s*)[a]	–	116.83 (*d*)	116.81 (*d*)
4″	150.62 (*s*)[b]	150.63 (*s*)	–	161.39 (*s*)	161.35 (*s*)
5″	116.42 (*d*)[c]	116.45 (*d*)[b]	–	116.83 (*d*)	116.81 (*d*)
6″	124.30 (*d*)	124.36 (*d*)	–	133.82 (*d*)	131.30 (*d*)
OMe	56.48 (*q*)[d]	56.50 (*q*)[c]	–	–	–
$3-X$					
α‴	147.20 (*d*)	148.27 (*d*)	147.98 (*d*)	148.28 (*d*)	148.29 (*d*)
β‴	114.26 (*d*)	114.45 (*d*)	114.48 (*d*)	114.40 (*d*)	114.48 (*d*)
γ‴	167.82 (*s*)	168.18 (*s*)	168.04 (*s*)	167.97 (*s*)	168.19 (*s*)
1‴	127.38 (*s*)	127.52 (*s*)	127.48 (*s*)	127.51 (*s*)	127.54 (*s*)
2‴	111.77 (*s*)	119.52 (*d*)	111.74 (*d*)	111.88 (*d*)	111.94 (*d*)
3‴	149.37 (*s*)[a]	149.35 (*s*)[a]	149.44 (*s*)[a]	149.41 (*s*)[a]	149.37 (*s*)
4‴	150.98 (*s*)	150.89 (*s*)	150.96 (*s*)	151.09 (*s*)	150.92 (*s*)
5‴	116.37 (*d*)[c]	116.79 (*d*)[b]	116.54 (*d*)	116.51 (*d*)	116.45 (*d*)
6‴	124.49 (*d*)	124.45 (*d*)	124.51 (*d*)	124.62 (*d*)	124.51 (*d*)
OMe	56.46 (*q*)[d]	56.43 (*q*)[c]	56.56 (*q*)	50.57 (*q*)[b]	56.51 (*q*)[a]
$6-X$					
α⁗	147.50 (*d*)	147.48 (*d*)	147.16 (*d*)	147.30 (*d*)	147.21 (*d*)
β⁗	115.05 (*d*)	115.20 (*d*)	115.18 (*d*)	115.16 (*d*)	115.21 (*d*)
γ⁗	168.66 (*s*)	168.80 (*s*)	168.80 (*s*)	168.79 (*s*)	168.81 (*s*)
1⁗	127.48 (*s*)	127.57 (*s*)	127.68 (*s*)	127.74 (*s*)	127.77 (*s*)
2⁗	111.63 (*d*)	111.73 (*d*)	111.62 (*d*)	111.68 (*d*)	111.73 (*d*)
3⁗	149.28 (*s*)[a]	149.83 (*s*)[a]	149.36 (*s*)[a]	149.50 (*s*)[a]	149.37 (*s*)
4⁗	150.66 (*s*)[b]	150.70 (*s*)	150.66 (*s*)	150.73 (*s*)	150.67 (*s*)
5⁗	116.48 (*d*)[c]	116.45 (*d*)[b]	116.54 (*d*)	116.58 (*d*)	116.45 (*d*)
6⁗	124.24 (*d*)	124.25 (*d*)	124.23 (*d*)	124.33 (*d*)	124.28 (*d*)
OMe	56.35 (*q*)[d]	56.40 (*q*)[c]	56.56 (*q*)	50.54 (*q*)[b]	56.51 (*q*)[a]

FABMS m/z: $[M - H]^-$ 953.2743 (Calcd. for $C_{46}H_{49}O_{22}$: 953.2723), ^1H and ^{13}C-NMR spectral data: Tables 1 and 2.

Smiglaside C (**3**): amorphous powder, $[\alpha]_D$: 32.86° (MeOH; *c* 0.6). UV λ_{max} (MeOH) nm (log ε): 217 (4.27), 328 (4.42), IR ν_{max} (KBr) cm^{-1}: 3400, 1745, 1710, 1620, 1500, 1220, 1020 cm^{-1}, negative ion FABMS m/z: 819 $[M - H]^-$, HR-FABMS m/z: $[M - H]^-$ 819.2374 (Calcd. for $C_{38}H_{43}O_{20}$: 819.2342), ^1H and ^{13}C-NMR spectral data: Tables 1 and 2.

Smiglaside D (**4**): amorphous powder, $[\alpha]_D$: 67.14° (MeOH; *c* 0.5), UV λ_{max} (MeOH) nm (log ε): 217 (4.45), 324 (4.64), IR ν_{max} (KBr) cm^{-1}: 3400, 1740, 1720, 1700, 1600, 1500, 1140, 1040 cm^{-1}, negative ion FABMS m/z: 965 $[M - H]^-$, HR-FABMS m/z: $[M - H]^-$ 965.2658 (Calcd. for $C_{47}H_{49}O_{22}$: 965.2717), ^1H and ^{13}C-NMR spectral data: Tables 1 and 2.

Smiglaside E (**5**): amorphous powder, $[\alpha]_D$: 123.84° (MeOH; *c* 0.4), UV λ_{max} (MeOH) nm (log ε): 217 (4.46), 323 (4.62), IR ν_{max} (KBr) cm^{-1}: 3450, 1740, 1720, 1710, 1690, 1600, 1520, 1260, 1040 cm^{-1}, negative ion FABMS m/z: 923 $[M - H]^-$, HR-FABMS m/z: $[M - H]^-$ 923.2606 (Calcd. for $C_{45}H_{47}O_{21}$: 923.2611), ^1H and ^{13}C-NMR spectral data: Tables 1 and 2.

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