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THREE PHENYLETHANOID GLYCOSIDES AND AN IRIDOID GLYCOSIDE FROM *PICRORHIZA SCROPHULARIIFLORA*

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Key Word Index—*Picrorhiza scrophulariiflora*; Scrophulariaceae; underground parts; phenylethanoid glycoside; iridoid glycoside; scroside; picroside.

Abstract—Three new phenylethanoid glycosides, named scrosides A–C and a new iridoid glycoside, named picroside IV, have been isolated from the underground parts of *Picrorhiza scrophulariiflora*, together with 11 known compounds. Their structures were elucidated by the means of 2D NMR spectroscopy and chemical methods. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Picrorhiza rhizoma, the underground part (mostly rhizome) of *Picrorhiza kurrooa*, has been extensively used in Ayurvedic medicine as a bitter tonic, an antiperiodic and a cholagogue. Many phytochemical studies on this species have been carried out and 44 compounds have been reported as constituents [1–4]. Another species, *P. scrophulariiflora*, was found in the high altitude region (over 4400 m) in south east Tibet and north west of Yunnan Province of China in 1965 [5]. This plant is now officially listed in the Chinese Pharmacopoeia and widely used for the treatment of damp-heat dysentery, jaundice and steaming of bone [6]. However, only a few papers have reported on its constituents [5, 7].

Herein, we wish to report the isolation and structural elucidation of three new phenylethanoid glycosides, named scrosides A (**1**), B (**2**) and C (**3**) and a new iridoid glycoside, named picroside IV (**4**).

RESULTS AND DISCUSSION

Dried and powdered underground parts of *P. scrophulariiflora* were extracted with hot MeOH. The MeOH extract was suspended in H_2O and partitioned successively between hexane, EtOAc, BuOH and H_2O. The BuOH portion was separated as described in Experimental and four new compounds **1–4** were isolated, together with the 11 known compounds, specioside [8], picroside I [9], picroside II [10], verminoside [11], minecoside [11], veronicoside [12], catalpol [10], 6-feruloylcatalpol [2], 2-(β-D-glucopyranosyloxy)-3,16,20,25-tetrahydroxy-9-methyl-19-norlanosta-5-ene-22-one [3], 2-(β-D-glucopyranosyloxy)-3,16,20-trihydroxy-9-methyl-19-norlanosta-5,24-diene-22-one [4] and plantamajoside [13].

Scroside A (**1**), a yellow amorphous powder, showed $[\alpha]_D$ −14.8° (MeOH) and its molecular formula was determined as $C_{37}H_{49}O_{21}$ by high resolution FAB-mass spectrometry. The UV spectrum showed absorptions at 202, 217, 288, 297 and 325 nm and in the IR spectrum absorptions attributable to a conjugated ester group (1770 and 1660 cm^{-1}) were observed. The ^1H and ^{13}C NMR spectra of **1**, extensively analyzed with the aid of DEPT, ^1H-^1H COSY and HMQC showed signals due to an ethyloxyl group, 15 oxymethines, including three anomers, three oxymethylenes, a *trans*-double bond, two 1,3,4-trisubstituted phenyl groups and two methoxyl groups (Tables 1 and 2). These data suggested that **1** should be a phenylethanoid glycoside [14, 15] containing a cinnamic acid residue, a phenylethyl moiety and three hexoses. The hexoses were determined to be three glucoses because acid hydrolysis with 0.5 N HCl yielded only glucose. Sugar proton and carbon signals were assigned by detailed analysis of ^1H-^1H COSY, HOHAHA and HMQC.

Next, HMBC and difference NOE experiments were employed in order to determine their connectivities. As shown in Fig. 1, the long-range correlations, C-4/OMe (δ 3.67) and C-3′/OMe (δ 3.78) in the HMBC spectrum, together with NOEs between OMe (δ 3.67) and H-5 and between OMe (δ 3.78) and H-2′, indicated that the aglycone was 3-hydroxy-4-methoxyphenylethyl alcohol and the ester group, feru-

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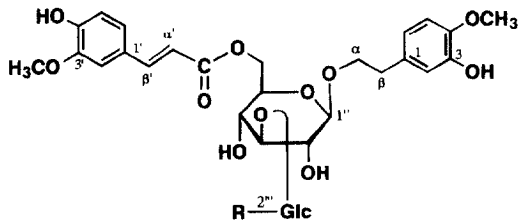

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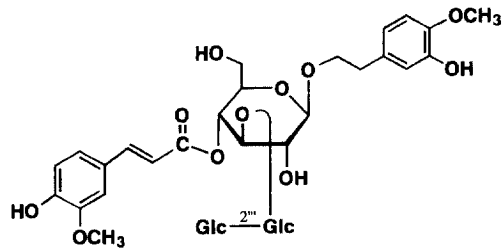

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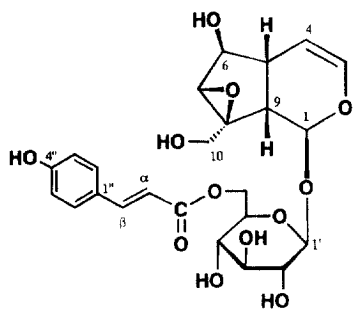

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Structure 1.

loyl. Likewise, the correlations, C=O/H_2-6″, enabled us to assign the position of the feruloyl group to C-6″ of glucose-1. Moreover, the clear correlations, C-3″/H-1‴ and C-2‴/H-1⁗, indicated that glucose-2 should be attached to C-3″ of glucose-1 and glucose-3 to C-2‴ of glucose-2. This was supported by difference NOE experiment, i.e. irradiation of the anomeric protons of glucose-2 (H-1‴) and glucose-3 (H-1⁗) enhanced the signal intensities of H-3″ and H-2‴, respectively. On the basis of the above findings, the structure of scroside A was determined to be **1**, which was further confirmed by detailed analysis of the difference ROE and ^{1}H-^{1}H COSY spectra of acetate **1a** (Table 1).

Scroside B (**2**) was obtained as an amorphous powder and showed $[\alpha]_D$ −11.1° (MeOH). It exhibited a *pseudo*-molecular ion peak at *m/z* 667 $[M-H]^-$ in the FAB-mass spectrum. The ^{1}H NMR spectrum of **2** and analysis by ^{1}H-^{1}H COSY, exhibited two anomeric protons at δ 4.88 (*d*, J = 7.8 Hz) and 5.38 (*d*, J = 8.0 Hz), while complete acid hydrolysis afforded only glucose. On the other hand, comparison between the ^{13}C NMR spectra of **2** and **1**, revealed the disappearance of a set of glucose signals and a large upfield shift of the C-2‴ signal of glucose-2 (**2** δ 75.68; **1** δ 85.82), indicating that glucose-3 in **1** was absent in **2**. This was further supported by HMBC and NOE experiments. Thus, the structure of scroside B was concluded to be **2**.

Scroside C (**3**), a yellow amorphous powder, showed $[\alpha]_D$ −45.0° (MeOH) and its HR-FAB-mass spectrum indicated that it had the same molecular formula as **1**. The ^{1}H and ^{13}C NMR spectra of **3** were similar to those of **1** (Tables 1 and 2) and detailed analyses of ^{1}H-^{1}H COSY, HOHAHA and HMQC spectra suggested that it was an isomer of **1**. The ^{1}H NMR spectrum showed a marked downfield shift (δ

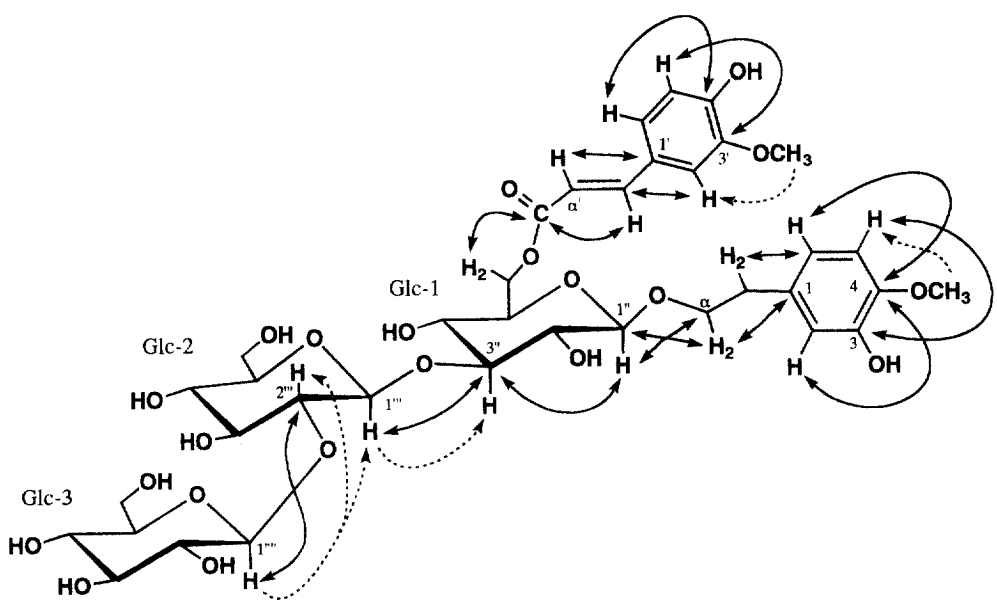

Fig. 1. Significant HMBC (solid arrow) and NOE (dashed arrow) correlations for scroside A (**1**).

Table 1. ^{1}H NMR spectral data of scrosides A (**1**), B (**2**), C(**3**) and scroside A acetate (**1a**)

H	1	1a	2	3
Aglycone				
2	7.16 (*d*, *J* = 1.5)	7.11 (*d*, *J* = 2.0)	7.17 (*d*, *J* = 2.0)	7.14 (*d*, *J* = 1.5)
5	6.84 (*d*, *J* = 8.5)	6.92 (*d*, *J* = 8.5)	6.83 (*d*, *J* = 8.5)	6.89 (*d*, *J* = 8.5)
6	6.79 (*dd*, *J* = 8.5, 1.5)	7.09 (*dd*, *J* = 8.5, 2.0)	6.78 (*dd*, *J* = 8.5, 2.0)	6.76 (*dd*, *J* = 8.5, 1.5)
α	4.22*	4.15 (*m*)	4.33*	4.25*
	3.96*	3.70 (*m*)	3.96 (*q*, *J* = 7.5)	3.86*
β	2.98 (*t*, *J* = 7.5)	2.80 (*m*)	2.99 (*t*, *J* = 7.5)	2.97 (*t*, *J* = 7.5)
OCH_3	3.67 (*s*)	3.69 (*s*)	3.69 (*s*)	3.71 (*s*)
Feruloyl				
2′	7.26 (*d*, *J* = 1.5)	7.56 (*d*, *J* = 1.5)	7.27 (*s*)	7.59 (*s*)
5′	7.18 (*dd*, *J* = 8.3, 1.5)	7.22 (*d*, *J* = 8.5)	7.18 (*d*, *J* = 8.5)	7.17(*d*, *J* = 8.3)
6′	7.19 (*dd*, *J* = 8.3, 1.5)	7.29 (*dd*, *J* = 8.5, 1.5)	7.20 (*d*, *J* = 8.5)	7.33 (*d*, *J* = 8.3)
α'	6.67 (*d*, *J* = 16.0)	6.95 (*d*, *J* = 16.0)	6.68 (*d*, *J* = 16.0)	7.06 (*d*, *J* = 16.0)
β'	7.97 (*d*, *J* = 16.0)	7.97 (*d*, *J* = 16.0)	7.98 (*d*, *J* = 16.0)	8.07 (*d*, *J* = 16.0)
OCH_3'	3.78 (*s*)	3.85 (*s*)	3.78 (*s*)	3.86 (*s*)
Sugar moiety				
Glucose-1				
1″	4.88 (*d*, *J* = 8.0)	4.66 (*d*, *J* = 8.2)	4.88 (*d*, *J* = 7.8)	4.90 (*d*, *J* = 7.5)
2″	4.15 (*t*, *J* = 8.0)	5.70 (*dd*, *J* = 9.0, 8.2)	4.09*	4.22*
3″	3.99*	4.22 (*t*, *J* = 9.0)	4.28 (*t*, *J* = 9.0)	4.23*
4″	3.96*	5.54 (*d*, *J* = 9.0)	4.24 (*t*, *J* = 9.0)	5.72 (*t*, *J* = 9.0)
5″	3.94*	4.07 (*m*)	4.05 (*m*)	3.98*
6″	4.98 (*d*, *J* = 12.0)	4.75 (*dd*, *J* = 12.0, 3.5)	5.02 (*d*, *J* = 12.0)	4.48 (*d*, *J* = 12.0)
	4.80 (*dd*, *J* = 12.0, 2.2)	4.63 (*dd*, *J* = 12.0, 4.5)	4.90 (*dd*, *J* = 12.0, 2.0)	4.29*
Glucose-2				
1‴	5.15 (*d*, *J* = 7.8)	4.91 (*d*, *J* = 8.0)	5.38 (*d*, *J* = 8.0)	5.21 (*d*, *J* = 8.0)
2‴	4.11*	3.73 (*dd*, *J* = 9.5, 8.0)	4.12 (*dd*, *J* = 9.0, 8.0)	4.01 (*t*, *J* = 8.0)
3‴	4.32 (*t*, *J* = 9.0)	5.52 (*t*, *J* = 9.5)	4.26 (*t*, *J* = 9.0)	3.89*
4‴	4.17*	5.24 (*t*, *J* = 9.5)	4.06*	4.07 (*t*, *J* = 9.0)
5‴	4.03*	3.98 (*ddd*, *J* = 9.5, 4.5, 2.0)	4.04*	3.82*
6‴	4.57 (*d*, *J* = 12.0)	4.63 (*dd*, *J* = 12.0, 2.0)	4.56 (*dd*, *J* = 12.0, 2.2)	4.48 (*d*, *J* = 12.0)
	4.24*	4.29 (*dd*, *J* = 12.0, 4.5)	4.35 (*d*, *J* = 12.0)	4.18*
Glucose-3				
1⁗	5.26 (*d*, *J* = 7.8)	4.86 (*d*, *J* = 8.0)	—	5.25 (*d*, *J* = 8.0)
2⁗	4.09 (*dd*, *J* = 9.0, 7.8)	5.58 (*dd*, *J* = 9.0, 8.0)	—	4.03 (*t*, *J* = 8.0)
3⁗	4.22*	5.69 (*t*, *J* = 9.0)	—	4.18*
4⁗	4.30 (*t*, *J* = 9.0)	5.74 (*t*, *J* = 9.0)	—	4.20*
5⁗	3.96*	4.04 (*m*)	—	3.89*
6⁗	4.54 (*d*, *J* = 12.0)	4.78 (*dd*, *J* = 12.0, 3.5)	—	4.54 (*d*, *J* = 11.5)
	4.41 (*dd*, *J* = 12.0, 4.5)	4.56 (*dd*, *J* = 12.0, 2.0)		4.42 (*dd*, *J* = 11.5, 4.5)
$COCH_3$		2.48, 2.33, 2.30, 2.27, 2.26, 2.16, 2.08, 2.07, 2.01, 1.98, 1.95	—	—

δ values in pyridine-d_5 and coupling constants in Hz. *Signal pattern unclear due to overlapping.

5.72) of H-4″ and significant upfield shift of H-6″ (δ 4.48 and 4.29) for glucose-1, compared with those of **1**, suggesting that the feruloyl moiety should be attached to the 4″-position. Moreover, the clear long-range correlations C=O/H-4″ in the HMBC spectrum of **3** further confirmed the position of the feruloyl moiety at C-4″ of glucose-1. Acid hydrolysis and HMBC and NOE experiments, showed that the sugar sequence was the same as that in **1**. These data allowed us to determine the structure of scroside C to be **3**.

Picroside IV (**4**) was isolated as a yellow amorphous powder with a molecular formula $C_{25}H_{27}O_{12}$. The IR spectrum showed absorption bands for a hydroxyl group at 3350 cm^{-1}, a conjugated ester carbonyl at 1720 cm^{-1} and a double band at 1650 cm^{-1}. The ^{1}H and ^{13}C NMR spectra (Table 3), coupled with the detailed analysis of the ^{1}H-^{1}H COSY and HMQC spectra, indicated the presence of an iridoid aglycone, a *para*-coumaroyl group and a hexose, which was characterized as glucose by comparison of NMR spectral data with those in literature [8]. These spectral data were similar to those of picroside III [16], except

Table 2. ^{13}C NMR spectral data of scrosides A (**1**), B (**2**) and C (**3**)

C	1	2	3
Aglycone			
1	132.3 (*s*)	132.1 (*s*)	132.3 (*s*)
2	117.6 (*d*)	117.5 (*d*)	117.6 (*d*)
3	148.0 (*s*)	148.0 (*s*)	148.0 (*s*)
4	147.1 (*s*)	147.1 (*s*)	147.2 (*s*)
5	112.6 (*d*)	112.6 (*d*)	112.7 (*d*)
6	120.1 (*d*)	119.9 (*d*)	120.1 (*d*)
α	71.1 (*t*)	71.1 (*t*)	71.1 (*t*)
β	36.2 (*t*)	36.1 (*t*)	36.1 (*t*)
OCH_3	55.9 (*q*)	55.9 (*q*)	56.0 (*q*)
Feruloyl			
1′	126.5 (*s*)	125.3 (*s*)	126.8 (*s*)
2′	111.4 (*d*)	111.2 (*d*)	111.5 (*d*)
3′	148.9 (*s*)	149.3 (*s*)	149.1 (*s*)
4′	150.1 (*s*)	150.1 (*s*)	151.1 (*s*)
5′	116.8 (*d*)	117.0 (*d*)	116.7 (*d*)
6′	123.8 (*d*)	124.2 (*d*)	124.0 (*d*)
α′	115.1 (*d*)	114.2 (*d*)	115.9 (*d*)
β′	145.8 (*d*)	146.0 (*d*)	146.0 (*d*)
CO	167.4 (*s*)	167.6 (*s*)	167.4 (*s*)
OCH_3′	55.9 (*q*)	55.8 (*s*)	55.9 (*q*)
Sugar moiety			
Glucose-1			
1″	103.2 (*d*)	104.2 (*d*)	103.2 (*d*)
2″	73.1 (*d*)	73.8 (*d*)	74.4 (*d*)
3″	90.9 (*d*)	88.1 (*d*)	86.2 (*d*)
4″	69.7 (*d*)	69.8 (*d*)	70.3 (*d*)
5″	74.6 (*d*)	74.8 (*d*)	76.4 (*d*)
6″	64.1 (*t*)	64.1 (*t*)	62.6 (*t*)
Glucose-2			
1‴	103.9 (*d*)	105.8 (*d*)	104.6 (*d*)
2‴	85.8 (*d*)	75.7 (*d*)	85.3 (*d*)
3‴	77.6 (*d*)	78.2 (*d*)	77.6 (*d*)
4‴	71.2 (*d*)	71.6 (*d*)	71.2 (*d*)
5‴	78.5 (*d*)	78.6 (*d*)	78.1 (*d*)
6‴	62.3 (*t*)	62.4 (*t*)	62.2 (*t*)
Glucose-3			
1⁗	107.1 (*d*)	—	106.4 (*d*)
2⁗	76.4 (*d*)	—	76.7 (*d*)
3⁗	77.9 (*d*)	—	77.6 (*d*)
4⁗	70.9 (*d*)	—	70.9 (*d*)
5⁗	79.2 (*d*)	—	79.0 (*d*)
6⁗	62.3 (*t*)	—	62.2 (*t*)

δ value in pyridine-d_5. The multiplicities of carbon signals were determined by the distortionless enhancement by polarization transfer (DEPT) method and are indicated as *s*, *d*, *t* and *q*.

for the absence of a methoxyl signal. Furthermore, the long-range correlations H_2-6′/C=O and C-1/H-1′ in the HMBC spectrum (Fig. 2) suggested that the *para*-coumaroyl group should be located at C-6′ of glucose and the glucose at C-1 of the iridoid aglycone. These long-range correlations together with others shown by arrows in Fig. 2 led us to establish the structure of picroside IV as **4**.

EXPERIMENTAL

General

IR spectra were recorded using KBr disks. Optical rotations were measured in MeOH solutions at 25°. FAB-MS and HR-FAB-MS data were obtained using glycerol + *m*-nitrobenzyl alcohol as matrix. ^1H and ^{13}C NMR spectra were taken on a JEOL JNM-Lambda 400WB spectrometer in pyridine-d_5 with TMS as int. standard; chemical shifts are recorded as δ values. ^1H-^1H COSY, HOHAHA, ^1H-^{13}C COSY and HMBC spectra were obtained with the usual pulse sequences and data processing was performed with standard JEOL software. CC was performed using Wakogel C-200 or Cosmosil 75C_{18}-OPN columns. TLC was carried out on precoated silica gel F_{254} plates (0.25 or 0.5 mm) or Merck RP-18 F_{254} reverse-phase plates (0.25 mm) and spots were detected under UV light or by spraying with $Ce(SO_4)_2$–10% H_2SO_4 (1:99).

Plant material

Picrorhiza scrophulariiflora Pennell was purchased from Tochimoto Tenkaidou (Osaka, Japan) and identified by Dr Namba (Toyama Medical and Pharmaceutical University). A voucher sample is deposited at the Museum of Materia Medica, Analytical Research Center for Ethnomedicines of Toyama Medical and Pharmaceutical University, Toyama, Japan.

Extraction and isolation

Powdered underground parts (500 g) were extracted × 3 with MeOH under reflux. The MeOH extract (190 g) was suspended in H_2O and successively partitioned hexane, EtOAc and BuOH, to yield hexane (7.5 g), EtOAc (16.4 g), BuOH (93.0 g), and H_2O (35.0 g) extracts, respectively. The BuOH extract was subjected to silica gel CC, using mixts of $CHCl_3$–MeOH of increasing polarity to give frs 1–8.

Fr. 1 (3.1 g) was subjected to Cosmosil 75C_{18}-OPN CC eluting with MeOH–H_2O (7:3) to yield 2-(β-D-glucopyranosyloxy)-3,16,20-trihydroxy-9-methyl-19-norlanosta-5,24-diene-22-one (6 mg). Picroside I (5.0 g) was obtained from fr. 2 (36.8 g). Fr. 3 (11.4 g) was chromatographed over silica gel and eluted with $CHCl_3$–MeOH (7:3) to give picroside IV (**4**) (11 mg). Fr. 4 (12.0 g), on repeated silica gel and MCI gel CC, yielded catalpol (40 mg), 2-(β-D-glucopyranosyloxy)-3,16,20,25-tetrahydroxy-9-methyl-19-norlanosta-5-ene-22-one (10 mg) and veronicoside (8 mg). Frs 5 (16.1 g) and 6 (4.0 g) were purified by Cosmosil 75C_{18}-OPN CC and prep. TLC to give picroside II (5.0 g) and plantamajoside (27 mg), respectively. Fr. 7 (1.4 g) was separated on Cosmosil 75C_{18}-OPN CC, repeated prep. TLC and reverse-phase TLC to provide verminoside (40 mg), minecoside (17 mg), specioside (29 mg), 6-feruloylcatalpol (40 mg) and scroside B (**2**) (26

Table 3. ^1H and ^{13}C NMR spectral data of picroside IV (**4**)

	H	C		H	C
1	5.53 (*d*, *J* = 10.0)	95.4 (*d*)	3′	4.29 (*dd*, *J* = 9.0, 8.0)	78.1 (*d*)
3	6.46 (*dd*, *J* = 6.0, 1.5)	141.0 (*d*)	4′	4.18 (*t*, *J* = 9.0)	71.1 (*d*)
4	5.32 (*dd*, *J* = 6.0, 4.5)	104.2 (*d*)	5′	4.09 (*m*)	75.9 (*d*)
5	2.84 (*tdd*, *J* = 8.0, 4.5, 1.5)	39.2 (*d*)	6′	5.01 (*dd*, *J* = 12.0, 2.0)	63.8 (*t*)
6	4.32 (*d*, *J* = 8.0)	79.1 (*d*)		4.87 (*dd*, *J* = 12.0, 5.0)	
7	3.87 (*s*)	62.3 (*d*)	1″		126.1 (*s*)
8		66.1 (*s*)	2″, 6″	7.52 (*d*, *J* = 8.5)	130.7 (*d*)
9	2.92 (*dd*, *J* = 10.0, 8.0)	43.5 (*d*)	3″, 5″	7.11 (*d*, *J* = 8.5)	116.7 (*d*)
10	4.66 (*d*, *J* = 13.0)	60.9 (*t*)	4″		161.4 (*s*)
	4.46 (*d*, *J* = 13.0)		α	6.56 (*d*, *J* = 16.0)	115.0 (*d*)
1′	5.50 (*d*, *J* = 8.0)	100.4 (*d*)	β	7.94 (*d*, *J* = 16.0)	145.4 (*d*)
2′	4.16 (*t*, *J* = 8.0)	74.9 (*d*)	CO		167.4 (*s*)

δ values in pyridine-d_5 and coupling constants in Hz. The multiplicities of carbon signals were determined by the distortionless enhancement by polarization transfer (DEPT) method and are indicated as *s*, *d*, *t*, and *q*.

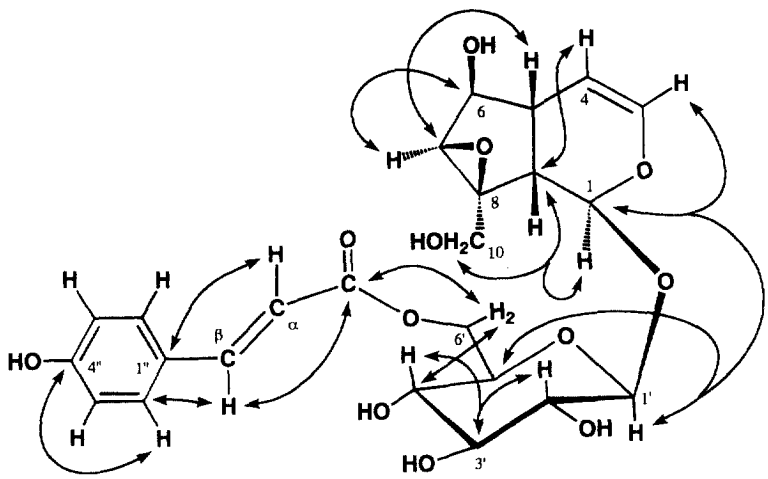

Fig. 2. Significant HMBC correlations for picroside IV (**4**).

mg). Fr. 8 (3.0 g) on repeated Cosmosil 75C_{18}-OPN and MCI gel CC gave scroside A (**1**) (40 mg) and scroside C (**3**) (20 mg).

Scroside A (**1**). Yellow amorphous powder. $[\alpha]_D$ −14.8° (MeOH; *c* 0.12). UV λ_{max} (MeOH) nm (log ε): 202 (4.35), 217 (3.91), 288 (3.75), 297 (3.73), 325 (3.86). IR ν_{max} (KBr) cm^{-1}: 3400 (*br*), 1770, 1700, 1660, 1580, 1500, 1440, 1340, 1230, 1190, 1140, 1100. Negative ion FAB-MS *m/z*: 829 $[M-H]^-$. HR-FAB-MS *m/z* 829.2726 $[M-H]^-$ (calcd for $C_{37}H_{49}O_{21}$: 829.2767). ^1H and ^{13}C NMR in Tables 1 and 2.

Scroside B (**2**). Yellow amorphous powder. $[\alpha]_D$ −11.1° (MeOH; *c* 0.12). UV λ_{max} (MeOH) nm (log ε): 203 (4.63), 217 (4.32), 288 (4.16), 326 (4.30). IR ν_{max} (KBr) cm^{-1}: 1335, 1690, 1620, 1580, 1500, 1420, 1260, 1150, 1120, 1070, 1020. Negative ion FAB-MS *m/z*: 667 $[M-H]^-$. ^1H and ^{13}C NMR in Tables 1 and 2.

Scroside C (**3**). Yellow amorphous powder. $[\alpha]_D$ −45.0° (MeOH; *c* 0.12). UV λ_{max} (MeOH) nm (log ε): 195 (4.30), 204 (4.82), 218 (4.52), 288 (4.34), 327 (4.48). IR ν_{max} (KBr) cm^{-1}: 3450, 1720, 1640, 1600, 1520, 1440, 1380, 1280, 1160, 1130, 1080, 1040. Negative ion FAB-MS *m/z*: 829 $[M-H]^-$. HR-FAB-MS *m/z*: 829.2740 $[M-H]^-$ (calcd for $C_{37}H_{49}O_{21}$: 829.2766). ^1H and ^{13}C NMR in Tables 1 and 2.

Picroside IV (**4**). Yellow amorphous powder. $[\alpha]_D$ −84.8° (MeOH; *c* 0.08). UV λ_{max} (MeOH) nm (log ε): 195 (4.12), 203 (4.50), 227 (4.33), 313 (4.58), 377 (2.57). IR ν_{max} (KBr) cm^{-1}: 1720, 1650, 1600, 1580, 1210. Negative ion FAB-MS *m/z*: $[M-H]^-$. HR-FAB-MS *m/z*: 507.1503 $[M-H]^-$ (calcd for $C_{24}H_{27}O_{12}$: 507.1503). ^1H and ^{13}C NMR in Table 3.

Acid hydrolysis of compounds **1**–3

Compounds **1**–**3** (each 5 mg) were each hydrolyzed with 0.5 N HCl for 3 h at 100 °. After neutralization with NH_4OH, followed by extraction with EtOAc (20 ml × 3), the aq. layer was lyophilized to give a residue.

This was analyzed by TLC using EtOAc–MeOH–H_2O–HOAc (13:6:3:3) and glucose was identified ($R_f = 0.39$).

Acetylation of compound **1**

A mixt. of **1** (5 mg), Ac_2O (0.5 ml) and pyridine (1 ml) was left at room temp. for 12 h. After decomposition of excess reagent with H_2O, the reaction mixt. was extracted with EtOAc. The EtOAc extract was concd and separated by prep. TLC using hexane–EtOAc (2:3) to yield acetate **1a** (4.5 mg).

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