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CUCURBITANE GLYCOSIDES FROM *HEMSLEYA PANACIS-SCANDENS* RHIZOMES

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Key Word Index—*Hemsleya panacis-scandens*; Cucurbitaceae; rhizomes; cucurbitane glycosides; scandenosides R8–R11; scandenogenins D and E; perseapicroside A; sweet natural glycoside.

Abstract—From the rhizomes of *Hemsleya panacis-scandens*, four new cucurbitane glycosides and a known glycoside, perseapicroside A, were isolated. The structures of these new glycosides, named scandenosides R8–R11, were determined as the 3-*O*-*β*-D-glucopyranoside-26-*O*-*β*-D-glucopyranoside of 3*β*,26-dihydroxycucurbit-5-en-11-one, the 2-*O*-*β*-D-glucopyranoside of 2*β*,3α,16α-trihydroxy-22,23,24,25,26,27-hexanorcucurbit-5-ene-11,20-dione, the 3-*O*-*β*-D-glucopyranoside of 2*β*,3α,20(*S*),26,27-pentahydroxy-16α,23(*S*)-epoxycucurbita-5,24-dien-11-one and the 3-*O*-*β*-D-glucopyranoside-26-*O*-*β*-gentiobioside of 3*β*,11α,26-trihydroxy-5*β*,6*β*-epoxycucurbit-24-ene by spectroscopic and chemical methods. The structure of perseapicroside A was shown to be incorrect.

INTRODUCTION

As part of our ongoing study on glycosides of the rhizomes of Chinese *Hemsleya* species we reported the isolation and structural elucidation of oleanane glycosides from *H. macrosperma* and *H. chinensis* [1], and cucurbitane glycosides from *H. carnosiflora* [2] and *H. panacis-scandens* [3]. Some of these cucurbitane glycosides taste sweet or bitter, and the structure–taste relationships of the glycosides of a 3*β*-hydroxy-cucurbit-5-ene-type triterpene were discussed [3].

Further examination of the rhizomes of *H. panacis-scandens* C. Y. Wu et Z. L. Chen afforded five additional cucurbitane glycosides. The present paper deals with the structural elucidation of these compounds.

RESULTS AND DISCUSSION

An ethanolic extract of the rhizomes of *H. panacis-scandens* was suspended in water and the suspension was extracted successively with ether, ethyl acetate and 1-butanol. The butanol layer was chromatographed on a column of a highly porous copolymer of styrene and divinylbenzene. The 95% ethanol eluate was repeatedly chromatographed to give five cucurbitane glycosides (**1**–**5**). Glycoside **5** tastes sweet and **2**–**4** taste bitter, while **1** is tasteless.

Inspection of the ^{1}H and ^{13}C NMR spectra of glycoside **1**, named scandenoside R8, suggested the presence of two *β*-glucopyranosyl units and carnosiflogenin A (**1a**, 3*β*,26-dihydroxycucurbit-5-en-11-one), which is a common aglycone of carnosiflosides I–III of *H. carnosiflora* [2]. The glycosylation shifts [4] were observed at the signals due to the C-3 and C-26 of **1** (Table 1). The evidence led to the formulation of **1** as carnosiflogenin A 3-*O*-*β*-D-glucopyranoside-26-*O*-*β*-D-glucopyranoside. This is the first time that **1** has been isolated in nature. However, this compound has already been obtained as a partially hydrolysed product of carnosifloside III (3-*O*-*β*-D-glucopyranoside-26-*O*-*β*-gentiobioside of **1a**) by enzymic hydrolysis [2]. The physical and spectral data for **1** agreed with those for an authentic sample.

Glycosides **2** and **3** have the same molecular formula, $C_{30}H_{46}O_{10}$, based on ^{13}C NMR and HR-FAB mass spectrometry. D-Glucose was identified in the acid hydrolysate of both glycosides. The NMR spectra showed that **2** and **3** are mono-*β*-glucopyranosides and very similar to each other in their structure. Enzymic hydrolysis of **2** with crude pectinase and hydrolysis of **3** with *β*-glucosidase yielded a common aglycone **2a**, which is identical with hexanorcucurbitacin F (2*β*,3α,16α-trihydroxy-22,23,24,25,26,27-hexanorcucurbit-5-ene-11,20-dione), isolated from *Elaeocarpus dolichostylus* [5], by analyses of the spectral data. By comparing the ^{13}C NMR spectra of each glycoside with that of **2a** (Table 1), the glycosylation shifts were observed for the signals due to the C-2 (+ 12.3 ppm) of **2** and the C-3

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Table 1. ^{13}C NMR spectral data for glycosides and aglycones (in pyridine-d_5, 100 MHz)

C	1a*	1	2a	2	3	4a	4	5a	6*	5	C	1	2	3	4	5
1	21.2	22.0	34.7	33.3	33.8	34.6	33.8	24.3	25.8	24.9	2-*O*-					
2	29.7	28.3	71.0	83.3	78.7†	71.0	71.2	31.4	30.8	30.6	G-1		106.5			
3	75.5	87.1	81.5	80.7	93.8	81.5	93.8	78.5	76.3	87.1	G-2		75.9			
4	41.9	41.9	42.8	42.5	42.5	42.8	42.5	40.3	42.3	41.3	G-3		78.5			
5	141.1	141.2	142.5	141.6	141.8	142.5	141.9	68.0	144.2	67.1	G-4		71.3			
6	118.9	118.4	118.6	118.8	119.2	118.8	119.3	53.7	119.2	53.0	G-5		78.5			
7	24.2	24.0	24.3	24.1	24.2	24.2	24.2	23.2	24.6	23.5	G-6		62.4			
8	44.1	43.8	43.6	43.3	43.3	43.0	42.8	42.6	43.6	42.4	3-*O*-					
9	49.1	49.0	49.3†	49.0[a]	49.0[a]†	49.3	49.2	39.7	40.2	39.9	G-1	107.2		107.2	107.2	106.5
10	35.9	35.9	34.5	34.1	34.0	34.3	33.8	34.0	36.6	34.5	G-2	75.4[b]		76.3	76.3	75.7[a]
11	213.8	213.6	211.9	211.7	211.8	213.0	213.0	78.6	77.8	78.8	G-3	78.6[c]		78.7[b]	78.7[a]	78.8[b]
12	48.7	48.6	47.5	47.4	47.4	48.9	49.2	40.8	41.1	40.8	G-4	71.7		71.6	71.6	71.7[c]
13	49.1	49.0	50.5†	50.4	50.4†	48.7	48.7	46.4	47.4	46.3	G-5	78.4[c]		78.6[b]	78.6[a]	78.3
14	49.4	49.5	49.1	49.1[a]	49.1[a]	48.8	48.6	49.6	49.8	49.7	G-6	62.8		62.8	62.8	62.7
15	34.5	34.5	46.2	46.0	46.0	41.7	41.6	34.2	34.5	34.3	26-*O*-					
16	28.0	28.3	71.5	71.3	71.1	70.7	70.6	27.9	28.4	27.9	inner					
17	49.6	49.5	68.0	68.0	67.9	56.1	56.0	50.8	50.7	50.8	G-1	103.3				103.3
18	16.8[a]	16.8[a]	19.9	19.9	19.9	20.0	20.1	16.9	17.0	17.0	G-2	74.9[b]				75.2[a]
19	20.1	20.2	20.4	20.1	20.3	20.6	20.5	25.0	26.7	25.0	G-3	78.6[c]				78.3[b]
20	35.9	35.9	208.5	208.5	208.5	72.4	72.3	36.0	36.2	36.1	G-4	71.7				71.6[c]
21	18.2[a]	18.1[a]	31.7	31.7	31.6	30.1	30.1	18.7	18.8	18.7	G-5	78.2[c]				77.3
22	36.6	36.0				46.8	46.6	36.5	36.9	36.3	G-6	62.8				70.0
23	24.6	24.7				71.0	70.9	24.8	24.9	24.9	26-*O*-					
24	124.9	128.7				128.5	128.2	125.0	125.1	128.9	terminal					
25	136.1	132.1				142.5	142.6	136.4	136.1	132.1	G-1					105.4
26	68.0	75.3				65.1	64.9	68.0	68.1	78.5	G-2					75.0[a]
27	13.9	14.2				58.7	58.5	13.9	14.0	14.2	G-3					78.3[b]
28	18.4[a]	18.4[a]	19.3†	19.0	19.1†	21.3	21.3	20.6	19.3[a]	20.7	G-4					71.6[c]
29	27.9	28.0	22.4	22.2	23.3	22.3	23.3	21.4	27.3	21.4	G-5					78.2[b]
30	26.3[a]	25.8[a]	25.5†	25.2	25.3†	25.5	25.3	25.3	26.2[a]	25.8	G-6					62.7

*Data taken from ref. [2].

†Assignments are changed from ref. [6].

[a–c]Interchangeable assignments.

Table 2. ^{1}H–^{13}C Long-range correlations of **4a** and **5a** by HMBC (in pyridine-d_5)

4a		**5a**	
H	Correlated C	H	Correlated C
3.33 (H-3)	42.8 (C-4)	3.58 (H-3)	40.3 (C-4)
5.67 (H-6)	34.3 (C-10)	3.25 (H-6)	68.0 (C-5)
1.91 (H-8)	49.3 (C-9), 48.8 (C-14)	1.57 (H-8)	39.7 (C-9), 49.6 (C-14)
2.69 (H-10)	49.3 (C-9)	2.72 (H-10)	39.7 (C-9)
2.62 (H-12a)	213.0 (C-11), 48.7 (C-13)	1.59 (H-17)	46.4 (C-13)
3.11 (H-12b)	213.0 (C-11), 48.7 (C-13)	0.81 (H-18)	46.4 (C-13)
1.53 (H-15a)	48.7 (C-13), 48.8 (C-14)	1.49 (H-19)	39.7 (C-9), 78.6 (C-11)
1.80 (H-15b)	48.7 (C-13), 48.8 (C-14)	4.32 (H-26)	125.0 (C-24), 136.4 (C-25)
2.12 (H-17)	48.7 (C-13), 72.4 (C-20)	1.83 (H-27)	136.4 (C-25)
1.18 (H-18)	48.7 (C-13)	0.89 (H-28)	49.6 (C-14), 34.2 (C-15)
1.17 (H-19)	49.3 (C-9), 213.0 (C-11)	1.07 (H-29)	78.5 (C-3), 40.3 (C-4), 68.0 (C-5)
1.40 (H-21)	72.4 (C-20)	1.21 (H-30)	78.5 (C-3). 40.3 (C-4), 68.0 (C-5)
1.79 (H-22)	72.4 (C-20)		
5.18 (H-23)	70.7 (C-16)		
7.02 (H-24)	142.5 (C-25)		
4.63 (H-26)	142.5 (C-25)		
4.65 (H-27a)	142.5 (C-25)		
4.70 (H-27b)	142.5 (C-25)		
1.32 (H-28)	48.8 (C-14)		
1.23 (H-29)	42.8 (C-4), 142.5 (C-5)		
1.40 (H-30)	42.8 (C-4), 142.5 (C-5)		

(+ 12.3 ppm) of **3**. In addition to this, NOEs were observed between H-2 (δ4.28) and the anomeric H (δ5.18) in the NOE differential spectrum of **2**, and between H-3 (δ3.37) and the anomeric H (δ5.28) in that of **3**. Based on these results, the structures of **2** and **3** were determined as the 2-*O*- and 3-*O*-β-D-glucopyranosides of **2a**, respectively.

Perseapicroside A, which has the same structure as **2**, has been reported as a bitter principle of *Persea mexicana* [6]. However, there is no definite evidence in the literature to prove the position of the glucosyl linkage on the C-2 of perseapicroside A, and its ^{1}H and ^{13}C NMR spectral data and optical rotation are not identical to those for **2**, but agree with those for **3**. Therefore, we conclude that, for the structure of the 2-*O*-β-D-glucopyranoside of **2a**, our compound **2**, named scandenoside R9, is reasonable, and that perseapicroside A corresponds to our compound **3**.

Glycoside **4**, named scandenoside R10, has a molecular formula of $C_{36}H_{56}O_{12}$. Acid hydrolysis of **4** provided D-glucose. The signals due to a β-glucopyranosyl unit were observed in its ^{1}H and ^{13}C NMR spectra. Enzymic hydrolysis of **4** with β-glucosidase afforded a new aglycone **4a** ($C_{30}H_{46}O_7$), named scandenogenin D. The ^{13}C NMR spectrum of **4a** indicated the presence of one carbonyl, two trisubstituted double bonds, seven methylene (two of them bearing an oxygen), seven methine (four of them bearing an oxygen), five quaternary (one of them bearing an oxygen) and six methyl carbons. The detailed analyses of the ^{1}H–^{1}H COSY, HSQC and HMBC (Table 2) data led to the formulation of **4a**, except for its stereochemistry. The 13 carbon signals of **4a** closely matched those assigned to the A- and B-rings as well as the C-19, C-29 and C-30 of **2a** (Table 1), assuming that **4a** is a 2β,3α-dihydroxycucurbit-5-ene-type triterpene. The stereochemistry of the remaining C- and D-rings and the side chain of **4a** was determined by a NOE experiment (in the differential ROE) as shown in Fig. 1. On the basis of these results, the structure of **4a** is characterized as 2β,3α,20(*S*),26,27-pentahydroxy-16α,23(*S*)-epoxycucurbita-5, 24-dien-11-one. The glycosyl linkage on C-3 of **4** was consistently supported when the ^{13}C NMR spectrum of **4** and **4a** were compared, taking the glycosylation shifts into consideration. The structure of **4** is thus determined as shown.

Glycoside **5**, named scandenoside R11, has a molecular formula $C_{48}H_{80}O_{19}$. The ^{1}H and ^{13}C NMR spectra of **5** demonstrated the presence of three monosaccharide units. Acid hydrolysis of **5** liberated D-glucose. Enzymic hydrolysis of **5** with a mixture of β-glucosidase and crude hesperidinase gave a new aglycone **5a** ($C_{30}H_{50}O_4$), named scandenogenin E. The 30 carbon signals of **5a** revealed one trisubstituted double bond, nine methylene (one of them bearing oxygen), seven methine (three of them bearing oxygen), five quaternary (one of them bearing oxygen) and seven methyl carbons (Table 1). Three oxygens were characterized as hydroxyl groups, and one was due to an epoxy group in consideration of the ^{13}C NMR data and molecular formula of **5a**. The ^{1}H–^{1}H COSY, HSQC and HMBC (Table 2) experiments allowed us to propose the plane structure of **5a**. The 13 carbon signals of **5a** appeared almost at the same positions as those assigned to the C-14–C-18 and side chain of carnosiflogenin C (**6**), which is an aglycone of carnosi-

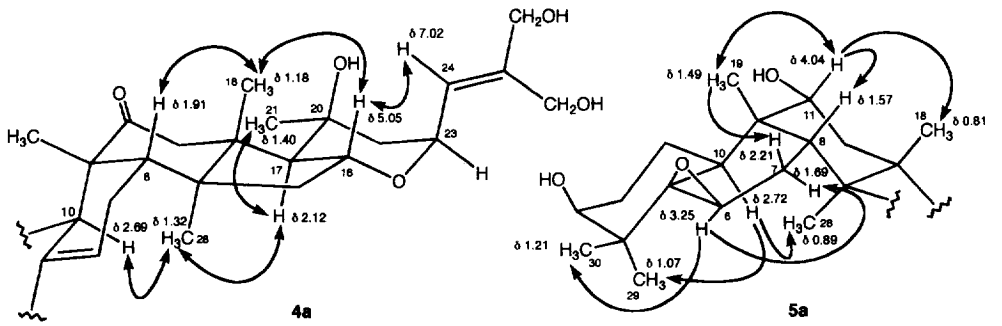
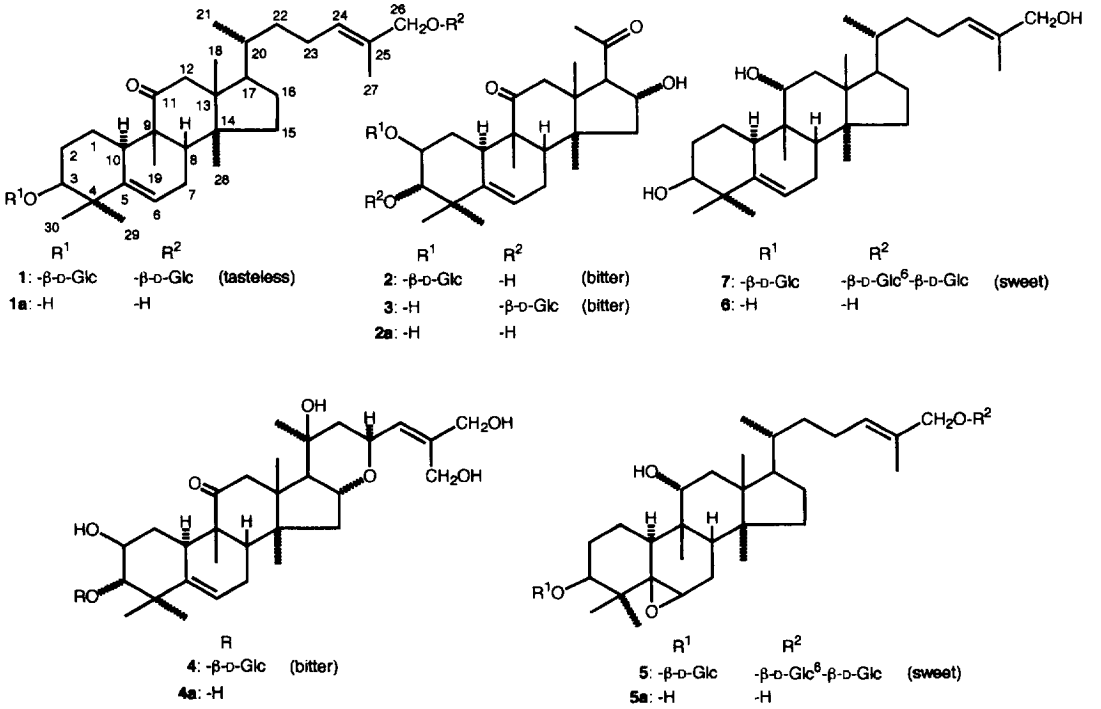


Fig. 1. NOE correlations of aglycones 4a and 5a.



floside VI (7) [2]. The orientations of the two hydroxyl groups at C-3 and C-11 were assigned as axial and equatorial, respectively, by the coupling constants and splitting patterns of the proton signals due to H-3 and H-11 (Table 3). The stereochemistry of the C-8–C-10, C-13, C-14 and epoxy group was substantiated by observation of NOEs in the differential ROE experiment of **5a**, as shown in Fig. 1. Based on these results, **5a** is characterized as 3β,11α,26-trihydroxy-5β,6β-epoxycucurbit-24-ene.

The ^{13}C NMR spectrum of **5** exhibited 18 peaks due to β-glucosyl and β-gentiobiosyl moieties in addition to signals consistent with an aglycone. The presence of these two sugar units were confirmed by a HOHAHA experiment with its acetate (**5–Ac**). A comparison of the ^{13}C NMR spectrum of **5** with that of **5a** displayed the glycosylation shifts at the signals attributed to C-3 and C-26, showing that **5** is the 3-*O*-glucosyl-26-*O*-gentiobiosyl or 3-*O*-gentiobiosyl-26-*O*-glucosyl compound of **5a**. The disposition of these two glycosyl linkages on **5a** was determined by a ROE experiment on **5–Ac**: selective irradiation of the anomeric proton signals at δ4.88 (gentiobiose) and 4.87 (glucose) caused distinct NOE enhancements for the signals due to the H-26a,b (δ4.14 and 4.37) and the H-3 (δ3.53) of aglycone, respectively. Accordingly, the structure of **5** is formulated as shown.

In our preceding paper [3], we proposed some structure–taste relationships for the glycosides of a 3β-hydroxycucurbit-5-ene-type triterpenoid. From the present study, an additional finding was obtained as follows. Scandenoside R11 (**5**) tastes sweet and is formulated as a 5,6-epoxy derivative of carnosifloside VI (**7**), which tastes sweet [2]. The corresponding 5,6-epoxy derivative of a sweet glycoside of a 3β-hydroxycucurbit-5-ene-type triterpenoid is thus retaining sweetness, but the relative sweetness of **5** could not be obtained because of the small amount of sample.

Table 3. ^{1}H NMR spectral data for aglycones **4a** and **5a** (in pyridine-d_5, 400 MHz)

H	4a	5a
1a	2.38 *ddd* (4, 4, 12)	2.90 *dddd* (3, 11, 11, 12)
1b	1.45 *ddd* (12, 12, 12)	3.08 *dddd* (3, 3, 3, 12)
2	4.00 *ddd* (4, 9, 12)	
2a		1.98 *dddd* (3, 3, 3, 13)
2b		2.15 m
3	3.33 *d* (9)	3.58 *br s*
6	5.67 *br d* (6)	3.25 *d* (6)
7a	1.83 *dd* (6, 19)	1.69 *dd* (6, 16)
7b	2.27 *dddd* (1, 1, 8, 19)	2.21 *dd* (8, 16)
8	1.91 *d* (8)	1.57 *d* (8)
10	2.69 *br d* (12)	2.72 *dd* (3, 11)
11		4.04 *dd* (5, 12)
12a	2.62 *d* (15)	2.13 *dd* (12, 13)
12b	3.11 *d* (15)	2.05 *dd* (5, 13)
15a	1.53 *dd* (3, 13)	1.02 *m*
15b	1.80 *dd* (10, 13)	1.15 *m*
16	5.05 *ddd* (3, 10, 10)	
16a		1.89 *m*
16b		obsc.
17	2.12 *d* (10)	1.59 *m*
18	1.18 *s*	0.81 *s*
19	1.17 *s*	1.49 *s*
20		obsc.
21	1.40 *s*	0.95 *d* (6)
22a	1.79 *d* (14)	1.18 *m*
22b	obsc.	1.52 *m*
23	5.18 *d* (7, 7)	
23a		2.05 *m*
23b		2.23 *m*
24	7.02 *d* (7)	5.74 *ddtq* (7, 7, 1, 1)
26	4.63 *s*	4.32 *d* (1)
27		1.83 *d* (1)
27a	4.65 *d* (13)	
27b	4.70 *d* (13)	
28	1.32 *s*	0.89 *s*
29	1.23 *s*	1.07 *s*
30	1.40 *s*	1.21 *s*

The chemical shifts for the protons at C-2, C-15, C-16, C-17, C-22 and C-23 in **5a** were obtained approximately from the HSQC.

J (Hz) in parentheses.

EXPERIMENTAL

General. Mps: uncorr.; ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in pyridine-d_5 with TMS as int. standard.; CC: silica gel (Kieselgel 60, 70–230 mesh, Merck) and silanized silica gel (LiChroprep RP-18, 40–63 μm, Merck) were used. All solvent systems for chromatography were homogeneous. HPLC: D-ODS-10 S-10 120A (YMC, Japan). Acid hydrolysis of glycosides and identification of resulting monosaccharides: see ref. [7].

Plant material. Hemsleya panacis-scandens C. Y. Wu et Z. L. Chen was cultivated and harvested in the Botanical Garden of Kunming Institute of Botany, Yunnan, China and authenticated by Emeritus Professor Cheng-Yih Wu of this Institute. A specimen has been deposited in the Herbarium of the Institute.

Extraction and separation. Dried and powdered rhizomes of *H. panacis-scandens* (1.1 kg) were extracted with EtOH, and the EtOH extract (352 g) was concd to dryness. The residue was suspended in H_2O, and then extracted with Et_2O, EtOAc and 1-BuOH, successively. The 1-BuOH extract was chromarographed on a column of highly porous copolymer of styrene and divinylbenzene (DA-201, China) and eluted with H_2O, 95% EtOH and EtOH, successively. The fr. eluted with 95% EtOH (73 g) was sepd into 15 frs by CC on silica gel with $CHCl_3$–MeOH–H_2O (10:5:1). Frs 3 (1.5 g) and 13 (5 g) were subjected to CC on RP-8 (65% MeOH) to afford **2** (463 mg) and **3** (117 mg) from fr. 3 and **5** (335 mg) from fr. 13. Fr. 4 (2 g) gave **1** (30 mg) and **4** (187 mg) by CC on RP-8 (65% MeOH) and then HPLC (72% MeOH).

Scandenoside R8 (**1**). Powder, $[\alpha]_D^{25}$ + 54° (MeOH; *c* 1.5), lit. + 66.5° [2]. ^{1}H NMR: δ4.90 (1H, *d*, *J* = 8 Hz, anomeric H), 4.85 (1H, *d*, *J* = 8 Hz, anomeric H). ^{13}C NMR: Table 1.

Scandenoside R9 (**2**) (*hexanorcucurbitacin F* 2-O-β-D-*glucopyranoside*). Powder, $[\alpha]_D^{25}$ + 119° (MeOH; *c* 1.1). FAB-MS (negative) *m/z* 565.3052, $C_{30}H_{45}O_{10}$ requires: *m/z* 565.3013. ^{1}H NMR: δ5.68 (1H, *d*, *J* = 5 Hz, H-6), 5.32 (1H, *br dd*, *J* = 7, 7 Hz, H-16), 5.18 (1H, *d*, *J* = 8 Hz, Glc-1), 4.46 (1H, *dd*, *J* = 2, 12 Hz, Glc-6a), 4.36 (1H, *dd*, *J* = 5, 12 Hz, Glc-6b), 4.28 (1H, *dd*, *J* = 9, 12 Hz, Glc-4), 4.28 (1H, *ddd*, *J* = 4, 9, 9 Hz, H-2), 4.17 (1H, *dd*, *J* = 9, 9 Hz, Glc-3), 4.07 (1H, *dd*, *J* = 8, 9 Hz, Glc-2), 3.84 (1H, *ddd*, *J* = 2, 5, 12 Hz, Glc-5), 3.52 (1H, *d*, *J* = 9 Hz, H-3), 3.44 (1H, *d*, *J* = 6 Hz, H-17), 3.13 (1H, *d*, *J* = 14 Hz, H-12a) 2.79 (1H, *br d*, *J* = 13 Hz, H-10), 2.51 (1H, *ddd*, *J* = 4, 4, 12 Hz, H-1a), 2.40 (1H, *d*, *J* = 14 Hz, H-12b), 2.29 (1H, *ddd*, *J* = 5, 8, 19 Hz, H-7a), 2.09 (3H, *s*, H-21), 1.88 (1H, *dd*, *J* = 5, 19 Hz, H-7b), 1.83 (1H, *d*, *J* = 8 Hz, H-8), 1.78 (1H, *br d*, *J* = 13 Hz, H-15a), 1.52 (3H, *s*, H-28), 1.44 (3H, *s*, H-30), 1.32 (3H, *s*, H-29), 1.15 (3H, *s*, H-19), 0.73 (3H, *s*, H-18). ^{13}C NMR: Table 1.

Enzymic hydrolysis of scandenoside R9 (**2**). Crude pectinase (Tanabe, Japan, 150 mg) was added to a soln of **2** (95 mg) in 20% EtOH (5 ml) and the mixt. was incubated for 25 hr at 37°. The reaction mixt. was subjected to CC on highly porous copolymer of styrene and divinylbenzene (DIAION HP-20, H_2O and then MeOH). The MeOH eluate was subjected to CC on silica gel to afford **2a** (24 mg).

Hexanorcucurbitacin F (**2a**). Prisms, mp 238–240° (MeOH), lit. [6] mp 237.5–238° (EtOH), $[\alpha]_D^{28}$ + 182° ($CHCl_3$; *c* 0.28), lit. $[\alpha]_D^{25}$ + 140° ($CHCl_3$; *c* 0.18) [5]. ^{13}C NMR: Table 1.

Hexanorcucurbitacin F 3-O-β-D-glucopyranoside (**3**). Powder, $[\alpha]_D^{25}$ + 103° (MeOH; *c* 1.1). FAB-MS (negative) *m/z* 565.3002, $C_{30}H_{45}O_{10}$ requires: *m/z* 565.3013. ^{1}H NMR: δ5.69 (1H, *d*, *J* = 5 Hz, H-6), 5.32 (1H, *br dd*, *J* = 8, 8 Hz, H-16), 5.28 (1H, *d*, *J* = 8 Hz Glc-1), 4.54 (1H, *dd*, *J* = 2, 12 Hz, Glc-6a), 4.43 (1H, *dd*, *J* = 5, 12 Hz, Glc-6b), 4.28 (1H, *ddd*, *J* = 4, 9, 9 Hz, H-2), 3.93 (1H, *ddd*, *J* = 2, 4, 5 Hz, Glc-5), 4.13 (1H, *dd*, *J* = 8, 8 Hz, Glc-2), 4.17 (1H, *dd*, *J* = 9, 9 Hz, Glc-

3), 3.44 (1H, *d*, $J = 8$ Hz, H-17), 3.37 (1H, *d*, $J = 9$ Hz, H-3), 3.26 (1H, *d*, $J = 14$ Hz, H-12a), 2.36 (1H, *ddd*, $J = 4, 4, 12$ Hz, H-1a), 2.69 (1H, *br d*, $J = 13$ Hz, H-10), 2.30 (1H, *ddd*, $J = 5, 8, 19$ Hz, H-7a), 2.54 (1H, *d*, $J = 14$ Hz, H-12b), 2.12 (3H, *s*, H-21), 1.92 (1H, *dd*, $J = 5, 19$ Hz, H-7b), 1.86 (1H, *d*, $J = 8$ Hz, H-8), 1.78 (1H, *br d*, $J = 13$ Hz, H-15a), 1.53 (3H, *s*, H-28), 1.48 (3H, *s*, H-30), 1.23 (3H, *s*, H-29), 1.22 (3H, *s*, H-19), 0.76 (3H, *s*, H-18). ^{13}C NMR: Table 1. These data closely matched those described for perseapicroside A [6].

Enzymic hydrolysis of hexanorcucurbitacin F 3-O-β-D-glucopyranoside (**3**). An aq. soln (5 ml) of glycoside **3** (13 mg) and β-glucosidase (6 mg, Sigma, lot No. G-8625 from almonds) was incubated for 24 hr at 37°. The reaction mixt. was extracted with CH_2Cl_2. The organic layer was evapd to give **2a** (5 mg).

*Scandenoside R*10 (**4**). Powder, $[\alpha]_D^{25} + 131°$ (MeOH; *c* 0.79). FAB-MS (negative) *m/z* 679.3673, $C_{36}H_{55}O_{12}$ requires: *m/z* 679.3693. ^{1}H NMR: δ 7.14 (1H, *d*, $J = 8$ Hz, H-24), 5.68 (1H, *d*, $J = 6$ Hz, H-6), 5.23 (1H, *dd*, $J = 7, 7$ Hz, H-23), 5.18 (1H, *d*, $J = 8$ Hz, Glc-1), 5.11 (1H, *ddd*, $J = 3, 10, 10$ Hz, H-16), 4.76 (1H, *d*, $J = 12$ Hz, H-27a), 4.71 (2H, *s*, H-26), 4.71 (1H, *d*, $J = 12$ Hz, H-27b), 4.54 (1H, *dd*, $J = 2, 12$ Hz, Glc-6a), 4.42 (1H, *dd*, $J = 5, 12$ Hz, Glc-6b), 4.12 (1H, *dd*, $J = 8, 8$ Hz, Glc-2), 3.93 (1H, *ddd*, $J = 2, 5, 9$ Hz, Glc-5), 3.36 (1H, *d*, $J = 9$ Hz, H-3), 3.11 (1H, *d*, $J = 14$ Hz, H-12a), 2.62 (1H, *d*, $J = 14$ Hz, H-10), 2.62 (1H, *d*, $J = 14$ Hz, H-12b), 2.42 (1H, *ddd*, $J = 4, 4, 12$ Hz, H-1a), 2.28 (1H, *br dd*, $J = 8, 19$ Hz, H-7a), 2.13 (1H, *d*, $J = 10$ Hz, H-17), 1.98 (1H, *dd*, $J = 7, 14$ Hz, H-22a), 1.91 (1H, *d*, $J = 8$ Hz, H-8), 1.82 (1H, *d*, $J = 14$ Hz, H-22b), 1.56 (1H, *dd*, $J = 3, 10$ Hz, H-15a), 1.52 (3H, *s*, H-30), 1.42 (3H, *s*, H-21), 1.30 (3H, *s*, H-28), 1.23 (3H, *s*, H-19), 1.22 (3H, *s*, H-18), 1.20 (3H, *s*, H-29). ^{13}C NMR: Table 1.

*Enzymic hydrolysis of scandenoside R*10 (**4**). Glycoside **4** (52 mg) was hydrolysed with β-glucosidase (20 mg) by the same procedure as that of glycoside **3** to yield **4a** (33 mg).

Scandenogenin D (**4a**). Powder, $[\alpha]_D^{25} + 113°$ (MeOH; *c* 1.4). FAB-MS (negative) *m/z* 517.3170, $C_{30}H_{45}O_7$ requires: *m/z* 515.3165. ^{13}C NMR: Table 1. ^{1}H NMR: Table 3.

*Scandenoside R*11 (**5**). Powder, $[\alpha]_D^{19} - 9.7°$ (MeOH; *c* 0.86). FAB-MS (negative) *m/z* 959.5212, $C_{48}H_{79}O_{19}$ requires: *m/z* 959.5208. ^{1}H NMR: δ5.69 (1H, *br dd*, $J = 7, 7$ Hz, H-24), 5.12 (1H, *d*, $J = 8$ Hz, Glc-1), 4.87 (1H, *d*, $J = 8$ Hz, Glc-1′), 4.84 (1H, *d*, $J = 8$ Hz, Glc-1″), 3.71 (1H, *br s*, H-3), 3.17 (1H, *d*, $J = 6$ Hz, H-6), 3.05 (1H, *br d*, $J = 11$ Hz, H-1a), 2.67 (1H, *br d*, $J = 11$ Hz, H-10), 1.80 (3H, *s*, H-27), 1.48 (3H, *s*, H-19), 1.21 (3H, *s*, H-30), 1.19 (3H, *s*, H-29), 0.91 (3H, *d*, $J = 6$ Hz, H-21), 0.89 (3H, *s*, H-28), 0.81 (3H, *s*, H-18). ^{13}C NMR: Table 1.

*Enzymic hydrolysis of scandenoside R*11 (**5**). Crude hesperidinase (Tanabe, 68 mg) and β-glucosidase (Boehringer Monheim, lot No. 105 422 from sweet almond, 64 mg) was added to a soln of **5** (69 mg) in H_2O (5 ml) and the mixt. was incubated for 72 hr at 37°. The reaction mixt. was extracted with Et_2O. The Et_2O extract was subjected to CC on silica gel with *n*-hexane–EtOAc (1:1) and then purified by HPLC with 75% MeOH to give **5a** (13.6 mg).

Scandenogenin E (**5a**). Powder, $[\alpha]_D^{19} + 4.3°$ (MeOH; *c* 0.23). FAB-MS (negative) *m/z* 473.3611, $C_{30}H_{49}O_4$ requires: *m/z* 473.3591. ^{13}C NMR: Table 1. ^{1}H NMR: Table 3.

*Acetylation of scandenoside R*11 (**5**). Glycoside **5** (20 mg) was acetylated with Ac_2O (2 ml) and pyridine (2 ml) in the usual way to afford crude acetate which was purified by HPLC with 82% MeOH to give **5-Ac** (16 mg): powder, ^{1}H NMR: δ5.65 (1H, *dd*, $J = 10, 10$ Hz, 26-*O*-terminal Glc-3), 5.63 (1H, *dd*, $J = 10, 10$ Hz, 26-*O*-inner-Glc-3), 5.64 (1H, *dd*, $J = 10, 10$ Hz, 3-*O*-Glc-3), 5.58 (1H, *dd*, $J = 6, 8$ Hz, H-24), 5.43 (1H, *dd*, $J = 8, 10$ Hz, 3-*O*-Glc-2), 5.42 (1H, *dd*, $J = 8, 10$ Hz, 26-*O*-terminal-Glc-2), 5.40 (1H, *dd*, $J = 8, 10$ Hz, 26-*O*-inner-Glc-2), 5.40 (1H, *dd*, $J = 10, 10$ Hz, 26-*O*-terminal-Glc-4), 5.36 (1H, *dd*, $J = 10, 10$ Hz, 3-*O*-Glc-4), 5.31 (1H, *dd*, $J = 10, 10$ Hz, 26-*O*-inner-Glc-4), 5.21 (1H, *dd*, $J = 7, 10$ Hz, H-11), 5.01 (1H, *d*, $J = 8$ Hz, 26-*O*-terminal-Glc-1), 4.88 (1H, *d*, $J = 8$ Hz, 26-*O*-inner-Glc-1), 4.87 (1H, *d*, $J = 8$ Hz, 3-*O*-Glc-1), 4.52 (1H, *dd*, $J = 5, 12$ Hz, 3-*O*-Glc-6a), 4.49 (1H, *dd*, $J = 5, 12$ Hz, 26-*O*-terminal-Glc-6a), 4.37 (1H, *d*, $J = 12$ Hz, H-26a), 4.35 (1H, *dd*, $J = 2, 12$ Hz, 3-*O*-Glc-6b), 4.32 (1H, *dd*, $J = 2, 12$ Hz, 26-*O*-terminal-Glc-6b), 4.20 (1H, *dd*, $J = 2, 12$ Hz, 26-*O*-inner-Glc-6a), 4.14 (1H, *d*, $J = 12$ Hz, H-26b), 4.05 (1H, *ddd*, $J = 2, 7, 10$ Hz, 26-*O*-inner-Glc-5), 4.03 (1H, *ddd*, $J = 2, 5, 10$ Hz, 3-*O*-Glc-5), 4.03 (1H, *ddd*, $J = 2, 5, 10$ Hz, 26-*O*-terminal-Glc-5), 3.88 (1H, *dd*, $J = 7, 12$ Hz, 26-*O*-inner-Glc-6b), 3.53 (1H, *br s*, H-3), 3.08 (1H, *d*, $J = 6$ Hz, H-6), 2.56 (1H, *dd*, $J = 2, 10$ Hz, H-10), 1.92–2.13 (3H × 12, *s*, OAc), 1.70 (3H, *d*, $J = 1$ Hz, H-27), 1.61 (1H, *dd*, $J = 6, 16$ Hz, H-7a), 1.56 (1H, *d*, $J = 8$ Hz, H-8), 1.15 (3H, *s*, Me), 1.19 (3H, *s*, Me), 0.94 (3H, *s*, Me), 0.91 (3H, *s*, Me), 0.89 (3H, *d*, $J = 6$ Hz, H-21), 0.87 (3H, *s*, Me).

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