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Triterpenoid Saponins From *Dianthus chinensis*

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Abstract: Four novel triterpenoid saponins, dianchinenosides E, F, G and H have been isolated from the aerial parts of *Dianthus chinensis* L. Dianchinenosides E and F, G and H are diastereomers with the only difference being in the stereochemistry of the 1,2-propanediol residues esterified to the C-23 of their aglycones. Their structures including the absolute configuration of the 1,2-propanediol fragments were established by spectral and chemical evidence as well as chiral HPLC analysis.

The genus *Dianthus* (Caryophyllaceae) is widely distributed in the northeast district of China. About three species of *Dianthus* have been used in Chinese traditional medicine as diuretic and antiinflammatory agents.[1] More recently, we have reported the isolation and structure study of triterpenoid saponins, dianchinenosides A, B, C and D from the aerial parts of *D. chinensis*.[2,3] In the continuation of our research, we isolated four additional novel triterpenoid saponins, dianchinenosides E (**1**), F (**2**), G (**3**) and H (**4**) from this source. It's very interesting to note that dianchinenosides E and F, G and H are diastereomers with the only difference being in the stereochemistry of the 1,2-propanediol residues esterified to the C-23 of their aglycones. The chromatographic behavior of the pairs is almost the same. Repeated separation by a combination of open columns (silica gel) and medium-pressure (silica gel and ODS) columns resulted in two TLC homogeneous saponin mixtures, revealed by their NMR data. The final painstaking HPLC purification of the pairs was carried out successfully using an ODS column with the retention time prolonged to 120 min. for **1**, **2** and 140 min. for **3**, **4** (MeOH-H_2O, 75:25, 0.5 ml/min.). After extensive 2D-NMR studies combined with some chemical reactions and chiral HPLC analysis, their structures were elucidated to be: dianchinenoside E (**1**), 23-*O*-(*R*)-1,2-propanediol-(1→23)-gypsogenic acid-28-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranoside; dianchinenoside F (**2**), 23-*O*-(*S*)-1,2-propanediol-(1→23)-gypsogenic acid-28-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranoside; dianchinenoside G (**3**) 23-*O*-

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(*R*)-1,2-propanediol-(1→23)-gypsogenic acid-28-*O*-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside; dianchinenoside H (**4**) 23-*O*-(*S*)-1,2-propanediol-(1→23)-gypsogenic acid-28-*O*-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside.

RESULTS AND DISCUSSION

An aqueous ethanol extract of the dried aerial parts of *Dianthus chinensis* was partitioned between chloroform and water. The water layer was further extracted with ethyl acetate and *n*-butanol, successively. The *n*-butanol soluble fractions were chromatographed on Diaion HP-20 and silica gel, followed by repeated MPLC and HPLC purification to afford four minor saponins, dianchinenosides E (**1**) and F (**2**), G (**3**) and H (**4**).

Dianchinenoside E (**1**), an amorphous solid, mp 214-216°, $[\alpha]^{28}_{D}$ +5.1°, has a molecular formula of $C_{57}H_{92}O_{26}$ determined by its positive ion FABMS (at *m/z* 1215 $[M+Na]^+$) as well as ^{13}C, DEPT NMR spectra. Of the 57 carbons, 30 were assigned to the aglycone part, 24 to the oligosaccharide moiety, and the remaining 3 to a 1,2-propanediol group (Tables 1 and 2). The IR spectrum showed a hydroxyl band at 3405 cm^{-1} and an ester band at 1718 cm^{-1}. The ^{13}C NMR data for the aglycone part was assigned to gypsogenic acid, a very common aglycone of the triterpenoid glycosides from this genus.[4] The ^{13}C chemical shifts at δ 176.0 and 177.7 suggested that both of the carbonyl groups were in esterified states. The C-3 signal at δ 74.8 revealed that no sugars were connected at this point. The tetrasaccharide nature of compound **1** was manifested by its ^1H [δ 4.88 d (*J*=7.6 Hz), 5.15 d (7.6), 5.18 d (7.6), 6.05 d (7.9)] and ^{13}C [δ 94.3, 102.2, 105.2 (x2)] NMR data (Tables 1 and 2). Hydrolysis of dianchinenoside E (**1**) with 1N HCl in aqueous methanol afforded an aglycone (**5**), which was characterized as 23-*O*-1,2-propanediol gypsogenic acid by its MS, 1D and 2D-NMR analyses. The existence of the 1,2-propanediol fragment was clearly shown from its COSY and HETCOR spectra. The esterification of this fragment to the C-23 of the gypsogenic acid was determined from a strong HMBC correlation between δ 4.24 (2H, C_1-H of the 1,2-propanediol) and δ 177.7 (C-23) of **1** (Figure 1, Table 2). The sugar units were identified to be glucoses based on GLC comparison with an authentic sample. From the above evidence, it is clear that the four moles of glucoses in **1** were connected to C-28 of the aglycone through an ester bond. The sequence of the oligosaccharide chain was determined by a combination of COSY, HOHAHA, HETCOR, HMBC and Phase-sensitive NOESY experiments. Interpretation of the COSY and 2D-HOHAHA spectra delineated all the spin systems of each individual sugar. On the basis of the assigned protons, a HETCOR experiment enabled the assignment of the ^{13}C shifts of these sugars. From the completely assigned ^{13}C NMR data, the branched nature of the sugar moiety was evident, and the noticeable ^{13}C shift differences between inner sugars and terminal ones indicated that the glucose (designated as G) directly connected to C-28 was glycosylated at G-3 (Δ 9.9 ppm) and G-6 (Δ 6.7 ppm). Also, another inner glucose (G") was glycosylated at G"-2 (Δ 7.8 ppm). The linkage between these sugars was established using the following HMBC correlations: H-1 of G' with C-3 of G; H-1 of G" with C-6 of G; and H-1 of G"' with C-2 of G". In addition, a strong correction between H-1 of G and C-28 of the aglycone further verified the connection of

the tetrasaccharide chain to C-28 of the aglycone (Figure 1). Moreover, Information from a phase-sensitive NOESY experiments confirmed these assignments (Figure 2). All the monosaccharides in the pyranose form were determined from their ^{13}C NMR data. The β anomeric configurations for these sugars were judged from their large $^{3}J_{H1, H2}$ coupling constants (7-8 Hz). The absolute configurations of these sugars were chosen in keeping with those mostly encountered among plant glycosides.

In order to determine the stereochemistry of the propanediol moiety, several methods were tried to release the fragment of interest from the aglycone **5**. Hydrolysis with 1N HCl or 2N KOH in aqueous MeOH as well as alkaline treatment with 3% sodium methoxide in MeOH left this part intact. Finally, on reduction with lithium aluminum hydride ($LiAlH_4$), **5** yielded the desired product propanediol (**8**) and the corresponding reduced product of gypsogenic acid, 12-oleanene-3β, 23, 28-triol (**7**). In order to verify the structure of **7**, an already known triterpenoid glycoside, 3-*O*-α-L-arabinopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside from the same plant[3] was first hydrolyzed with 1N HCl and then reduced with $LiAlH_4$. The resultant product was shown to be the same with compound **7** in all respects (co-TLC, NMR, MS). The determination of the absolute configuration of the propanediol fragment was based upon the following principle. The primary tosylate esters of authentic *R*-(-)- and *S*-(+)-propane-1,2-diols were well resolved by HPLC analysis using a CHIRALCEL OC column and a hexane-2-propanol (95:5, 2.5 ml/min.) developing system. Therefore, **8** was converted to a primary tosylate ester (1,2-propanediol 1-tosylate) and then subjected to co-HPLC comparison with authentic samples. The HPLC result showed that the propanediol fragment in dianchinenoside E (**1**) possessed an *R* configuration. The foregoing evidence led to the elucidation of the structure of **1** as 23-*O*-(*R*)-1,2-propanediol-(1→23)-gypsogenic acid-28-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranoside.

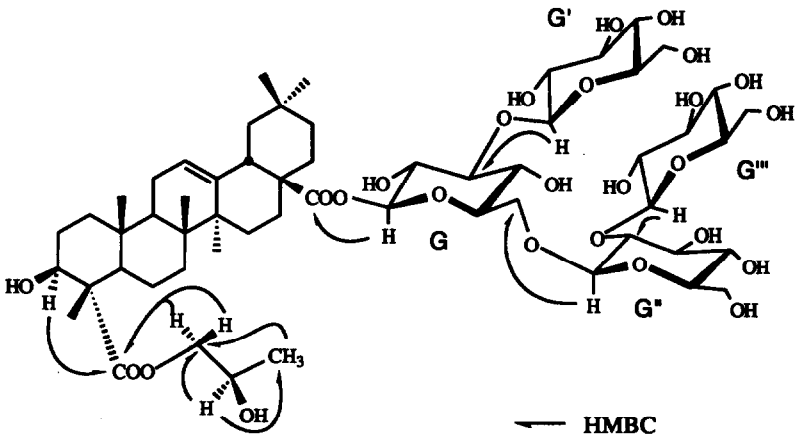


Figure 1. Some key HMBC correlations observed in Dianchinenoside E (**1**)

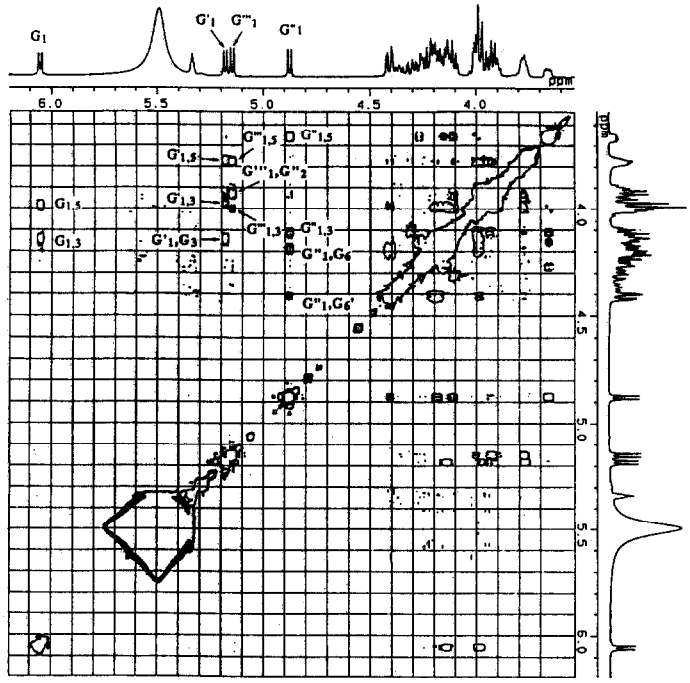


Figure 2 The Phase-sensitive NOESY for the Oligosaccharide Moiety of Dianchinenoside E (1).

Dianchinenoside F (2) is an amorphous solid, mp 215-218 °C, $[\alpha]_D$ +5.0°. Its FAB MS and NMR data indicated that compound 2 had the same molecular composition ($C_{57}H_{92}O_{26}$) and oligosaccharide chain as that of 1 but with a different configuration at the 1,2-propanediol parts. Such a stereochemical difference was clearly reflected from their ^1H NMR spectra (Table 2). After acidic hydrolysis and then $LiAlH_4$ reduction, compound 2 afforded 7 and the appropriate 1,2-propanediol unit (9). The latter was identified to be (*S*)-propane-1,2-diol using the same analytical procedure carried out for 1. Therefore, dianchinenoside F (2) was elucidated to be 23-*O*-(*S*)-1,2-propanediol-(1→23)-gypsogenic acid-28-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→6)-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranoside.

Dianchinenosides G (3) and H (4), amorphous solids, have a molecular formula of $C_{51}H_{82}O_{21}$. Their spectroscopic features suggested that both compounds were diasteromers with an opposite chiral center at the 1,2-propanediol fragment esterified to the C-23 of their aglycones. Detailed analysis of the ^1H and ^{13}C NMR data showed that both 3 and 4 contained a trisaccharide unit and their aglycone parts were the same as those of compounds 1 and 2 (gypsogenic acid) (Table 1). Acidic hydrolysis of 3 and 4 afforded 5 and 6, respectively, and the absolute configurations of the 1,2-propanediol fragments were determined using the same methods carried out for 1 and 2. The monosaccharides were identified to be glucoses based on GLC analysis, and the sequence of the oligosaccharide chain was determined by comparison of their ^{13}C NMR data with those of 1 and 2 as well as the long-range correlations from HMBC experiments. Accordingly, the structures of dianchinenosides G (3) and H (4) were established to be 23-*O*-(*R*)-1,2-

propanediol-(1→23)-gypsogenic acid-28-*O*-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside and 23-*O*-(*S*)-1,2-propanediol-(1→23)-gypsogenic acid-28-*O*-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside, respectively.

Dianchinenosides E (**1**), F (**2**), G (**3**) and H (**4**) are first natural products with 1,2-propanediol fragments linked to their aglycones. It's rather strange to see natural products incorporate such fragments into their molecules.

Table 1. ^{13}C NMR Data of the Aglycone Parts of Dianchinenosides E (**1**), F (**2**), G (**3**), H (**4**) and Aglycones **5**, **6** (125 MHz, pyridine-d_5)*

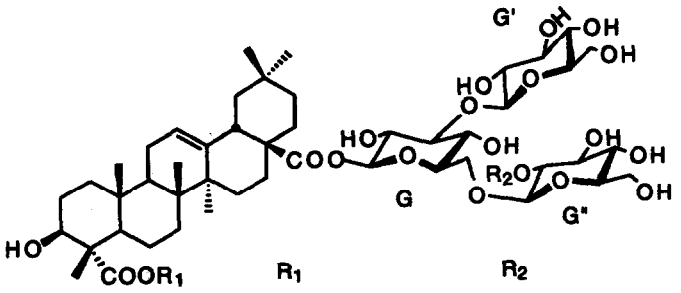
Carbon	1	2	3	4	5	6	DEPT
1	38.5	38.5	38.5	38.4	38.4	38.4	CH2
2	26.9	26.9	26.9	26.9	27.0	26.9	CH2
3	74.8	74.9	74.8	74.9	74.8	74.8	CH
4	54.4	54.4	54.4	54.4	54.5	54.4	C
5	51.5	51.5	51.5	51.5	51.5	51.5	CH
6	22.9	22.9	22.8	22.8	23.1	23.1	CH2
7	33.6	33.6	33.5	33.5	33.7	33.7	CH2
8	39.8	39.8	39.8	39.8	39.6	39.6	C
9	47.9	47.9	47.9	47.9	47.9	47.9	CH
10	36.4	36.4	36.3	36.3	36.3	36.3	C
11	23.4	23.4	23.4	23.4	23.3	23.3	CH2
12	122.3	122.3	123.3	122.2	122.0	121.9	CH
13	143.7	143.7	143.7	143.7	144.4	144.4	C
14	41.7	41.7	41.7	41.7	41.7	41.7	C
15	27.8	27.8	27.8	27.7	27.8	27.8	CH2
16	21.2	21.2	21.2	21.2	21.2	21.2	CH2
17	46.7	46.7	46.6	46.6	46.2	46.2	C
18	41.3	41.3	41.3	41.3	41.5	41.5	CH
19	45.8	45.9	45.8	45.8	46.1	46.0	CH2
20	30.3	30.3	30.3	30.3	30.5	30.5	C
21	32.3	32.3	32.3	32.3	32.7	32.7	CH2
22	32.0	32.1	31.9	31.9	32.4	32.4	CH2
23	177.7	177.7	177.7	177.7	177.7	177.7	C
24	11.2	11.3	11.3	11.3	11.3	11.3	CH3
25	15.6	15.6	15.6	15.6	15.5	15.5	CH3
26	16.9	17.0	16.9	16.9	16.8	16.8	CH3
27	25.5	25.6	25.5	25.5	25.6	25.6	CH3
28	176.0	176.0	176.0	175.9	179.8	179.8	C
29	32.6	32.6	32.6	32.6	32.8	32.8	CH3
30	23.2	23.2	23.2	23.2	23.2	23.2	CH3

*Assignments based on COSY, HOHAHA, DEPT, HETCOR and HMBC experiments

Table 2. ^{1}H and ^{13}C NMR Data for the Oligosaccharide Moieties of Dianchinenosides E (1) and F (2) (500 MHz for ^{1}H and 125 MHz for ^{13}C in pyridine-d_5)*

	Dianchinenoside E (1)		Dianchinenoside F (2)	
Sugar units	^{1}H shift	^{13}C shift	^{1}H shift	^{13}C shift
23-*O*-1,2-propanediol				
1	4.24 m	69.6 (t)	4.35 m	69.6 (t)
			4.14 m	
2	4.20 m	64.9 (d)	4.17 m	64.9 (d)
3	1.30 d	20.0 (q)	1.31 d	20.0 (q)
	(*J*=6.1 Hz)		(6.1 Hz)	
28-*O*-sugar				
G-1	6.05 d (7.9 Hz)	94.3 (d)	6.05 d (7.9 Hz)	94.3 (d)
G-2	4.12	72.7 (d)	4.12	72.6 (d)
G-3	4.14	87.4 (d)	4.15	87.4 (d)
G-4	4.21	68.6 (d)	4.21	68.6 (d)
G-5	3.98	76.4 (d)	3.98	76.4 (d)
G-6	4.19	68.5 (t)	4.19	68.5 (t)
	4.41		4.41	
G'-1	4.88 d (7.6)	105.2 (d)	4.87 d (7.9)	105.1 (d)
G'-2	3.92	75.1 (d)	3.92	75.0 (d)
G'-3	4.10	77.5 (d)	4.10	77.4 (d)
G'-4	3.99	70.7 (d)	3.98	70.7 (d)
G'-5	3.66 m	78.0 (d)	3.66 m	77.9 (d)
G'-6	4.16	61.8 (t)	4.16	61.8 (t)
	4.27		4.27	
G"-1	5.15 d (7.6)	102.2 (d)	5.14 d (7.6)	102.2 (d)
G"-2	3.90	82.9 (d)	3.90	82.9 (d)
G"-3	3.99	77.4 (d)	3.99	77.4 (d)
G"-4	3.99	70.6 (d)	3.99	70.5 (d)
G"-5	3.78 m	77.7 (d)	3.78 m	77.7 (d)
G"-6	4.20	61.7 (t)	4.20	61.7 (t)
	4.41		4.41	
G'''-1	5.18 d (7.6)	105.2 (d)	5.18 d (8.0)	105.1 (d)
G'''-2	3.91	75.7 (d)	3.91	75.7 (d)
G'''-3	3.97	77.3 (d)	3.97	77.3 (d)
G'''-4	3.97	70.3 (d)	3.97	70.3 (d)
G'''-5	3.77 m	77.9 (d)	3.77 m	77.8 (d)
G'''-6	4.11	61.9 (t)	4.10	61.9 (t)
	4.31		4.31	

*Assignments were based on COSY, HOHAHA, DEPT, HETCOR and HMBC experiments.



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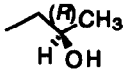
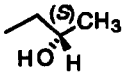
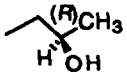
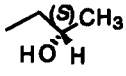
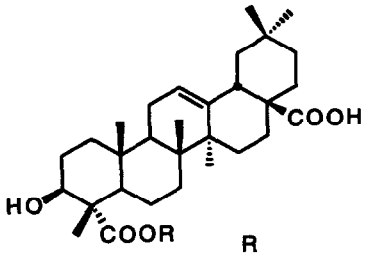
1		β-D-glc (G"')
2		β-D-glc (G"')
3		H
4		H



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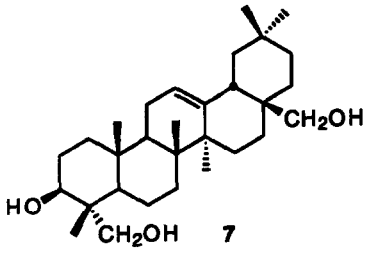

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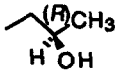
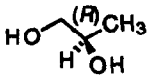
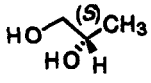
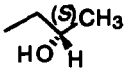
5			
6		8	9

EXPERIMENTAL

***General Procedures*:** All melting points were measured using a Yanaco microscope apparatus and are uncorrected. IR spectra were determined using a JASCO D-300 FTIR spectrometer. Optical rotations were measured using a JASCO DIP-370 digital polarimeter. EI and FABMS were conducted using JEOL D-300 and DX-303 mass spectrometers, respectively. ^1H and ^{13}C NMR were recorded using a JEOL α-500 FT-NMR or JEOL EX-400 FT-NMR spectrometer. Chemical shifts were expressed in δ (ppm) referring to solvent peaks: δ_H 7.20 and δ_C 135.50 for pyridine-d_5. Diaion HP-20 (Mitsubishi Kasei), silica gel (Silica gel 60, Merck), and ODS (Chromatorex, 100-200 mesh, Fujisylisia) were used for column chromatography. Preparative HPLC was performed using an ODS column (PEGASIL ODS, Senshu Pak, 10 mm i.d.x 250 mm, detector: UV 210 nm). GLC: 25 SE-30 on Chromsorb W (60-80 mesh), 3 mm i.d. x 1.5 m, 150 °C column temperature, N_2 carrier gas, 15 ml/min flow rate.

Extraction and Isolation of the Triterpenoid Saponins. Aerial parts of the plant, *Dianthus chinensis* L. were collected by one of the authors (H. Y. Li) from Dongliao, P. R. China, in September 1989. Dried aerial parts (7 kg) of *Dianthus chinensis* were extracted with 95%, 50% EtOH (10 liters, each) three times under reflux for 1 hr. The combined EtOH extract was concentrated under reduced pressure to an aqueous suspension, which was extracted with $CHCl_3$, EtOAc, and *n*-BuOH (500 ml, three times), successively. The *n*-BuOH extract (59 g) was applied to a column of Diaion HP-20 (4.5 kg) and washed with 30, 50, 70, and 100% MeOH. The fractions containing saponins were combined, and passed through a column of polyamide to eliminate flavonoids, and then chromatographed over silica gel and ODS columns to give several saponin fractions. The highly polar saponin fractions were further subjected to MPLC to give two TLC homogenous saponin mixtures, which were finally separated by HPLC with 75% MeOH-H_2O (0.5 ml/min) to afford dianchinenosides E (**1**, 47 mg), F (**2**, 58 mg), G (**3**, 90 mg) and H (**4**, 86 mg).

Dianchinenoside E (1). An amorphous solid, mp 214-216 °C, $[\alpha]^{28}_D$ +5.1° (MeOH; *c*=0.55). IR ν^{KBr}max cm^{-1}: 3405, 2940, 1718, 1654, 1074. FAB MS (positive ion mode) *m/z*: 1215 $[M+Na]^+$. ^1H-NMR (500 MHz, pyridine-d_5): δ 0.79, 0.81, 0.88, 0.96, 1.11, 1.41 (each 3H, s, H_3 of C-29, C-30, C-25, C-26 , C-27, C-24), 3.05 (1H, dd, *J*=13.5, 3.8 Hz, H-18), 4.36 (1H, m, H-3), 5.34 (1H, br.t, H-12). For other NMR data see, Tables 1 and 2.

Dianchinenoside F (2). An amorphous solid, mp 215-218 °C, $[\alpha]^{28}_D$ +5.0° (MeOH; *c*=0.20). IR ν^{KBr}max cm^{-1}: 3421, 2925, 1718, 1654, 1074. FAB MS (positive ion mode) *m/z*: 1193 $[M+H]^+$, 1215 $[M+Na]^+$, 1231 $[M+K]^+$. ^1H-NMR (500 MHz, pyridine-d_5): δ 0.79, 0.81, 0.88, 0.96, 1.11, 1.41 (each 3H, s, H_3 of C-29, C-30, C-25, C-26 , C-27, C-24), 3.05 (1H, dd, *J*=13.5, 3.8 Hz, H-18), 4.36 (1H, m, H-3), 5.34 (1H, br.t, H-12). For other NMR data, see Tables 1 and 2.

Dianchinenoside G (3). An amorphous solid, mp 202-204 °C, $[\alpha]^{28}_D$ +15.3° (MeOH; *c*=0.30). IR ν^{KBr}max cm^{-1}: 3405, 2940, 1727, 1697, 1074. FAB MS (positive ion mode) *m/z*: 1031 $[M+H]^+$, 1053

$[M+Na]^+$. ^{1}H-NMR (500 MHz, pyridine-d_5): δ 0.82 (x2), 0.90, 0.97, 1.12, 1.41 (each 3H, s, H_3 of C-29, C-30, C-25, C-26, C-27, C-24), 1.29 (3H, d, J=6.1 Hz, H_3-3, 1,2-prpopanediol), 3.05 (1H, dd, J=13.5, 3.8 Hz, H-18), 4.36 (1H, m, H-3), 4.83 (1H, d, J= 8.0 Hz, G"-H_1), 5.08 (1H, d, J= 7.9 Hz, G'-H_1), 5.34 (1H, br.t, H-12), 6.03 (1H, d, J=8.2 Hz, G-H_1). ^{13}C NMR data (125 MHz, pyridine-d_5): 95.4, 72.3, 87.8, 68.6, 77.1, 68.4 (G-1-G-6), 105.0, 74.9, 77.7, 70.9, 78.0, 62.1 (G'-1-G'-6), 104.8, 74.5, 77.5, 71.0, 77.8, 61.9 (G"-1-G"-6), 69.6 (CH_2), 64.9 (CH), 19.9 (CH_3) (C-1-C-3, 1,2-propanediol). For the ^{13}C NMR data for the aglycone part, see Table 1.

Dianchinenoside H (4). An amorphous solid, mp 198-200 °C, $[\alpha]^{28}_D$ +13.2° (MeOH; *c*=0.50). IR ν^{KBr}max cm $^{-1}$: 3423, 2940, 1720, 1654, 1074. FAB MS (positive ion mode) *m/z*: 1053 $[M+Na]^+$. ^{1}H-NMR (500 MHz, pyridine-d_5): δ 0.82 (x2), 0.90, 0.97, 1.12, 1.41 (each 3H, s, H_3 of C-29, C-30, C-25, C-26, C-27, C-24), 1.31 (3H, d, J=6.4 Hz, H_3-3, 1,2-propanediol), 3.05 (1H, dd, J=13.5, 3.8 Hz, H-18), 4.36 (1H, m, H-3), 4.83 (1H, d, J= 8.0 Hz, G"-H_1), 5.08 (1H, d, J= 7.9 Hz, G'-H_1), 5.34 (1H, br.t, H-12), 6.03 (1H, d, J=8.2 Hz, G-H_1). ^{13}C NMR data (125 MHz, pyridine-d_5): 95.4, 72.3, 87.8, 68.6, 77.1, 68.4 (G-1-G-6), 105.0, 74.9, 77.7, 70.9, 78.0, 62.1 (G'-1-G'-6), 104.8, 74.5, 77.5, 71.0, 77.8, 61.9 (G"-1-G"-6), 69.6 (CH_2), 64.9 (CH), 19.9 (CH_3) (C-1-C-3, 1,2-propanediol). For the ^{13}C NMR data for the aglycone part, see Table 1.

Acidic hydrolysis of Dianchinenosides E (1), F (2), G (3) and H (4). Compound **1** (10 mg) was heated in 1ml 1N HCl (MeOH-H_2O, 1:1) at 80 °C for 2 hr. in a water bath. After MeOH was removed, the solution was extracted with EtOAc (1 ml x 3). The extraction was washed with water and then combined to give an amorphous powder (**5**, 5 mg). The monosaccharide portion was neutralized by passing through an exchange resin (Amberlite MB-3) column, concentrated and then treated with 1-(trimethylsilyl) imidazole at room temperature for 2 hours. After the excess reagent was decomposed with water, the reaction product was extracted with hexane (1 ml x 3 times). The TMSi derivatives of the monosaccharides were identified to be D-glucoses by GLC analyses. Using the same method, **3** resulted in **5**, **2** and **4** afforded **6**, and the monosaccharides were shown to be D-glucoses by GLC analyses.

Aglycone 5. an amorphous solid, mp. 164-168 °C, $[\alpha]^{25}_D$+31.8° (MeOH; *c*=4.9). IRν^{KBr}max cm^{-1}: 3428, 2927, 1727, 1697, 1238, 1172, 1087. FAB MS (positive ion mode) *m/z*: 567 $[M+Na]^+$. EI MS (rel. int.) *m/z*: 527 $[M-OH]^+$(4.3), 499 $[M-COOH]^+$(4.1), 483 (4.2), 295 (25), 278 (42), 249 (100), 248 (100), 219 (41.0), 203 (100). ^{1}H NMR (400 MHz, pyridine-d_5): δ 0.84, 0.87, 0.89, 0.93, 1.16, 1.40 (3H, s, H_3 of C-29, C-30, C-25, C-26, C-27, C-24), 1.32 (3H, d, J=6.1 Hz, H_3-3, 1,2-propanediol), 3.16 (1H, dd, J=13.5, 3.6 Hz, H-18), 4.21 (1H, m, H-2, 1,2-propanediol), 4.25 (2H, m, H_2-1, 1,2-propanediol), 4.37 (1H, dd, J=9.3, 7.3, H-3), 5.37 (1H, br.t, H-12). ^{13}C NMR (100 MHz, pyridine-d_5): δ 69.6 (CH_2), 64.9 (CH), 20.0 (CH_3) (C-1-C-3, 1,2-propanediol). For other data, see Table 1.

Aglycone 6. an amorphous solid, mp. 156-158 °C, $[\alpha]^{25}_D$+47.4° (MeOH; *c*=9.2). IRν^{KBr}max cm^{-1}: 3424, 2931, 1720, 1697, 1238, 1163, 1087. FAB MS (positive ion mode) *m/z*: 567 $[M+Na]^+$. EI MS (rel. int.) *m/z*: 527 $[M-OH]^+$(1.1), 499 $[M-COOH]^+$(1.0), 483 (1.1), 295 (5.4), 278 (7.4), 249 (19),

248 (100), 219 (8.8), 203 (91). ^{1}H NMR (400 MHz, pyridine-d_5): δ 0.85, 0.88, 0.91, 0.93, 1.17, 1.42 (3H, s, H_3 of C-29, C-30, C-25, C-26, C-27, C-24), 1.33 (3H, d, J=6.1 Hz, H_3-3, 1,2-propanediol), 3.17 (1H, dd, J=14.0, 4.2 Hz, H-18), 4.17 (1H, dd, J= 10.6, 5.2 Hz, H_a-1, 1,2-propanediol), 4.21 (1H, m, H-2, 1,2-propanediol), 4.38 (1H, dd, J=10.6, 5.5 Hz, H_b-1, 1,2-propanediol), 4.40 (1H, m, H-3), 5.39 (1H, br.t, H-12). ^{13}C NMR (100 MHz, pyridine-d_5): δ 69.6 (CH_2), 64.9 (CH), 20.0 (CH_3) (C-1-C-3, 1,2-propanediol). For other data, see Table 1.

Reductive Cleavage of Compounds 5 and 6. A solution of **5** (5 mg) in anhydrous THF (5 ml) was treated with $LiAlH_4$ (20 mg) and the mixture was refluxed for 3 hr. After the excess $LiAlH_4$ was decomposed, the mixture was partitioned between $CHCl_3$ and H_2O. Purification of the product from the $CHCl_3$ layer afforded compound **7** (3.0 mg), FAB MS (positive ion mode) *m/z:* 459 $[M+H]^+$, ^{1}H NMR (400 MHz, pyridine-d_5): δ 0.92, 0.98, 0.99, 1.01, 1.09, 1.24 (3H, s, H_3 of C-29, C-30, C-25, C-26, C-27, C-24), 2.31 (1H, dd, J=13.5, 2.6 Hz, H-18), 3.58, 3.86 (each 1H, J=10.7 Hz, H_2 of C-28), 3.73, 4.20 (each, 1H, J=10.2 Hz, H_2 of C-23), 4.21(1H, dd, J=11.2, 4.9 Hz, H-3), 5.26 (1H, br.t, H-12). The water layer was concentrated in vacuum, dried and then esterified with *p*-toluenesulphonyl chloride in pyridine at room temperature for 30 min. The reaction product was subjected to co-HPLC comparison with the authentic *R*-(-)- and *S*-(+)-1,2-propanediol 1-tosylate to determine its absolute configuration. Using the same method, **6** afforded **7** and corresponding propanediol. *R*-(-)-1,2-propanediol 1-tosylate, thick oil. EI MS (rel. int.) *m/z*: 231 $[M+H]^+$ (8), 200 (36), 156 (80), 91(100). ^{1}H NMR (400 MHz in $CDCl_3$) δ 1.16 (3H, d, J=6.2 Hz, H_3-3), 2.46 (3H, s, H_3-4'), 3.85 (1H, dd, J=10.0, 7.1 Hz, H_a-1), 3.99 (1H, dd, J=10.0, 3.3 Hz, H_b-1), 4.03 (1H, m, H-2), 7.36 (2H, d, J=8.5 Hz, H-3', 5'), 7.80 (2H, d, J=8.5 Hz, H-2', 6'). *S*-(+)-1,2-propanediol 1-tosylate, thick oil. EI MS (rel. int.) *m/z*: 231 $[M+H]^+$ (11), 200 (30), 156 (85), 91(100). ^{1}H NMR (400 MHz in $CDCl_3$) δ 1.17 (3H, d, J=6.2 Hz, H_3-3), 2.46 (3H, s, H_3-4'), 3.85 (1H, dd, J=10.0, 7.2 Hz, H_a-1), 3.99 (1H, dd, J=10.0, 3.0 Hz, H_b-1), 4.04 (1H, m, H-2), 7.36 (2H, d, J=8.4 Hz, H-3', 5'), 7.80 (2H, d, J=8.4 Hz, H-2', 6'). HPLC conditions: column, CHIRALCEL OC (Daicel Chemical, Japan, 0.46 x 25 cm); solvent, hexane-2-propanol (95:5); flow rate, 2.5 ml/min; detection, UV 235 nm; retention time (R_t), *R*-(-)-1,2-propanediol 1-tosylate: 29.49 min, *S*-(+)-1,2-propanediol 1-tosylate: 33.48 min.

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