New Dammarane-Type Saponins from the Roots of *Panax notoginseng*

by **Li Qiu**[a][b][c], **Yang Jiao**[c], **Gui-Kun Huang**[c], **Ji-Zhao Xie**[c], **Jian-Hua Miao**[b], and **Xin-Sheng Yao***[a]

[a]) Institute of Traditional Chinese Medicine & Natural Products, Jinan University, Guangzhou 510632, Guangdong, P. R. China (phone/fax: +86-20-85225849; e-mail: tyaoxs@jnu.edu.cn)

[b]) Institute of Guangxi Medicinal Plant, Nanning 530023, Guangxi, P. R. China

[c]) School of Pharmaceutical Science, Guangxi Medical University, Nanning 530021, Guangxi, P. R. China

Three new dammarane-type triterpenoid saponins, **1**–**3**, were isolated and identified as (20*S*)-20-*O*-[β-D-xylopyranosyl-(1→6)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol (**1**), (20*S*)-6-*O*-[(*E*)-but-2-enoyl-(1→6)-β-D-glucopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol (**2**), and (20*S*)-6-*O*-[β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol (**3**) from the roots of *Panax notoginseng* (BURKILL) F.H.CHEN (Araliaceae). Their structures were elucidated on the basis of spectroscopic analyses, including 1D- and 2D-NMR techniques and HR-ESI-MS, as well as by acidic hydrolysis.

Introduction. – All saponins present in the roots of *Panax notoginseng*, as well as their derivatives, have been approved by the State Food and Drug Administration in China as clinical drugs, which are widely used in the prevention and treatment of cardiovascular diseases. Recent pharmaceutical studies have disclosed diverse bioactivities of the saponins from *Panax notoginseng*, such as anti-inflammatory [1][2], antitumor [3][4], antioxidant [5], hepatoprotective [6], immunomodulative, and immune-adjunctive activities [7]. A detailed phytochemical investigation of the root of *Panax notoginseng* was carried out in the present work. As a result, three new dammarane-type saponins, **1**–**3**, one natural compound, **7**, and other 20 known dammarane-type saponins, **4**–**6** and **8**–**24**, were isolated and identified, of which **14** and **15** were isolated for the first time.

Results and Discussion. – The 80% EtOH extract of the air-dried root of *Panax notoginseng* was chromatographed repeatedly to afford compounds **1**–**24** (*Figs. 1* and *2*). Three new minor saponins, **1**–**3**, and one new natural compound, 6′-*O*-acetylginsenoside Rh_1 (**7**) [8], along with 20 known compounds, 6-*O*-(β-D-glucopyranosyl)-20-*O*-(β-D-xylopyranosyl)-3β,6α,12β,20(*S*)-tetrahydroxydammar-24-ene (**4**) [9], (20*S*)-ginsenoside Rh_1 (**5**) [10], (20*R*)-ginsenoside Rh_1 (**6**) [11], (20*S*)-ginsenoside Rg_2 (**8**) [12], notoginsenoside-R_2 (**9**) [10], ginsenoside-F_1 (**10**) [13], ginsenoside Rg_1 (**11**) [14], notoginsenoside-R_1 (**12**) [10], ginsenoside Re (**13**) [15], (20*S*)-protopanaxatriol-20-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (**14**) [16], ginsenoside-Rh_4 (**15**) [17], vinaginsenoside R_4 (**16**) [18], (20*R*)-ginsenoside Rg_3 (**17**) [19], ginsenoside-Rd (**18**) [18], ginsenoside Rb_1 (**19**) [14], ginsenoside Ra_3 (**20**) [20][21], notoginsenoside

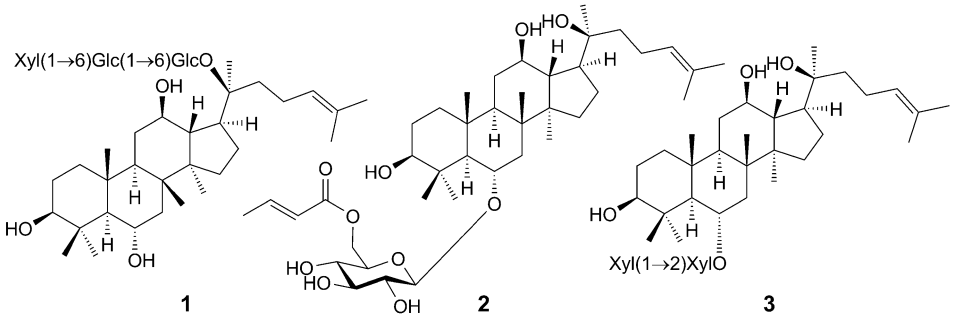
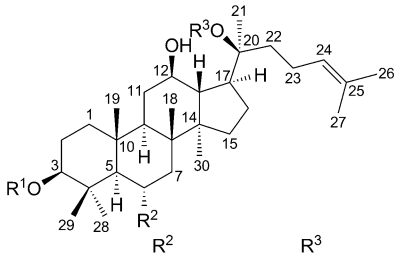


Fig. 1. *New compounds* **1**–**3** *isolated from the root of* Panax notoginseng



	R^1	R^2	R^3
4	H	GlcO	Xyl
5	H	GlcO	H
7	H	6'-AcGlcO	H
8	H	Rha(1→2)GlcO	H
9	H	Xyl(1→2)GlcO	H
10	H	OH	Glc
11	H	GlcO	Glc
12	H	Xyl(1→2)GlcO	Glc
13	H	Rha(1→2)GlcO	Glc
14	H	OH	Glc(1→6)Glc
16	Glc(1→2)Glc	OH	Glc
18	Glc(1→2)Glc	H	Glc
19	Glc(1→2)Glc	H	Glc(1→6)Glc
20	Glc(1→2)Glc	H	Xyl(1→3)Glc(1→6)Glc
21	Xyl(1→2)Glc(1→2)Glc	H	Glc(1→6)Glc
22	Glc(1→2)Glc	H	Xyl(1→3)Glc(1→6)Glc
23	Xyl(1→2)Glc(1→2)Glc	H	Xyl(1→3)Glc(1→6)Glc

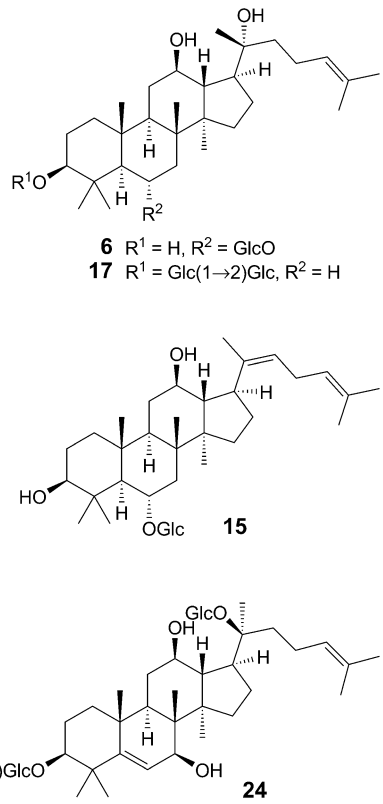


Fig. 2. *Chemical structures of* **4**–**24** *isolated from the root of* Panax notoginseng

Fa (**21**) [19], notoginsenoside R_4 (**22**) [14], notoginsenoside D (**23**) [22], and notoginsenoside-G (**24**) [23], were also isolated and identified by comparison of their

spectroscopic data with those reported in the literature. Among them, two known compounds, **14** and **15**, were isolated for the first time from *Panax notoginseng*.

Compound **1** was obtained as a white, amorphous powder. Its molecular formula was determined as $C_{47}H_{80}O_{18}$ by HR-ESI-MS (*m/z* 955.5229 ($[M+Na]^+$, $C_{47}H_{80}NaO_{18}^+$; calc. 955.5242)). The ^{1}H- and ^{13}C-NMR data (*Table*) of **1** were very similar to those of ginsenoside F_1 (**10**), except for two sets of signals due to a glucose and a xylose units. In the ^{1}H-NMR ((D$_5$)pyridine) spectrum of **1**, diagnostic signals were found for a sapogenin moiety with those of eight Me groups at δ(H) 0.97, 1.01, 1.09, 1.44, 1.60, 1.64, 1.64, 1.97 (each *s*, Me(30), Me(18), Me(19), Me(29), Me(26), Me(21), Me(27), Me(28), resp.), and of an olefinic H-atom at δ(H) 5.31 (*t*, $J = 6.2$, H–C(24)). In the ^{13}C-NMR spectrum of **1**, 47 C-atom signals were detected, including two olefinic C-atom signals of C(24) (δ(C) 126.0) and C(25) (δ(C) 131.0). The signals of C(5) and C(20) were shifted downfield to δ(C) 61.7 [24] and 83.4, respectively. In addition, the ^{1}H-NMR spectrum showed signals for three anomeric H-atoms at δ(H) 4.94 (*d*, $J = 7.5$, H–C(1‴)), 5.01 (*d*, $J = 7.7$, H–C(1″)), and 5.11 (*d*, $J = 7.8$, H–C(1′)), which showed HSQCs to anomeric C-atom signals at δ(C) 105.9 (C(1‴)), 105.5 (C(1″)) and 98.0 (C(1′)), respectively. Based on the coupling constants of the anomeric H-atoms, all sugar substituents were identified as β-configured.

Acid hydrolysis of **1** revealed the presence of xylose and glucose moieties, which were in relative proportions of 1:2, as determined by GC/MS analysis [25]. All these data suggested that compound **1** was a protopanaxatriol-type ginsenoside, and that the trisaccharide unit was attached to C(20). The exact oligoglycoside structure at C(20) in **1** was determined from the HMBC spectrum, which showed HMBCs from H–C(1′) (δ(H) 5.11) to C(20) (δ(C) 83.4), from H–C(1″) (δ(H) 5.01) to C(6′) (δ(C) 70.3), and from H–C(1‴) (δ(H) 4.94) to C(6″) (δ(C) 69.9) (*Fig. 3*). The relative configurations at the ring junctions were confirmed by a NOESY spectrum, which revealed the correlations from H–C(3) (δ(H) 3.48 – 3.53) to H–C(5) (δ(H) 1.20) and Me(28) (δ(H) 1.97), from H–C(6) (δ(H) 4.37 – 4.39) to Me(18) (δ(H) 1.01) and Me(19) (δ(H) 1.09), from H–C(12) (δ(H) 4.19 – 4.23) to H–C(9) (δ(H) 1.52 – 1.56) and Me(30) (δ(H) 0.97) (*Fig. 4*). The NOE correlation from Me(17) (δ(H) 2.57) to H–C(12) (δ(H) 4.19 – 4.23), Me(21) (δ(H) 1.64), and Me(30) (δ(H) 0.97) suggested that the configuration at C(20) should be (*S*). Furthermore, the HMBCs from Me(26) (δ(H) 1.60) and Me(27) (δ(H) 1.64) to C(24) (δ(C) 126.0) and from H–C(24) (δ(H) 5.31) to C(26) (δ(C) 25.8) and C(27) (δ(C) 17.9) confirmed that the C=C bond was located at the side train. The ^{1}H- and ^{13}C-NMR assignments for **1** were accomplished unambiguously based on HSQC, HMBC, and TOCSY data. Thus, the structure of **1** was determined as (20*S*)-20-*O*-[β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol.

Compound **2** was obtained as an amorphous powder. Its molecular formula was determined as $C_{40}H_{66}O_{10}$ by HR-ESI-MS (*m/z* 1413.9362 ($[2M+H]^+$, $C_{80}H_{133}O_{20}^+$; calc. 1413.9390)) and NMR data. The ^{1}H- and ^{13}C-NMR data (*Table*) of **2** were very similar to those of ginsenoside Rh_1 (**5**), except for a set of signals arising from the presence of a butenoyl unit. In the ^{1}H-NMR ((D$_5$)pyridine) spectrum of **2**, signals of eight Me groups at δ(H) 0.91, 1.04, 1.23, 1.41, 1.55, 1.61, 1.65, 2.01 (each *s*, Me(30), Me(19), Me(18), Me(21), Me(29), Me(26), Me(27), Me(28), resp.) and of an olefinic H-atom at δ(H) 5.31 (*t*, $J = 7.2$, H–C(24)) were displayed, and in the ^{13}C-NMR spectrum of **2**, 40 C-atom

Table. *^{1}H- and ^{13}C-NMR* (600 and 150 MHz, resp.) *Data of Compounds* **1**–**3**. In (D_5)pyridine; δ in ppm, J in Hz.

Position	**1**		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	0.99[a]), 1.70–1.74 (*m*)	39.3	1.69[a]), 1.00–1.03 (2*m*)	39.3	1.64–1.67, 0.97–1.00 (2*m*)	39.4
2	1.83[a]), 1.90–1.93 (*m*)	28.1	1.88–1.91, 1.81–1.85 (2*m*)	27.9	1.79–1.81, 1.82–1.86 (2*m*)	27.7
3	3.48–3.53 (*m*)	78.5	3.50 (br. *d*, *J* = 12.2)	78.6	3.45–3.49 (*m*)	78.6
4		40.3		40.2		40.0
5	1.20 (*d*, *J* = 10.4)	61.7	1.41–1.43 (*m*)	61.4	1.38[a])	61.2
6	4.37–4.39 (*m*)	67.7	4.38 (*td*, *J* = 10.5, 3.2)	80.0	4.32[a])	78.8
7	1.85[a]), 1.93–1.95 (*m*)	47.5	2.51 (*dd*, *J* = 12.6, 3.3), 1.93–1.97 (*m*)	45.6	1.93 (*t*, *J* = 11.6), 2.27[a])	45.3
8		41.2		41.2		41.1
9	1.52–1.56 (*m*)	49.9	1.57[a])	50.1	1.52[a])	50.0
10		39.3		39.7		39.6
11	1.59[a]), 2.04–2.09 (*m*)	30.8	2.12–2.16 (*m*), 1.55[a])	32.1	2.09–2.12 (*m*), 1.51[a])	32.0
12	4.19–4.23 (*m*)	70.1	3.90–3.94 (*m*)	71.0	3.90 (*t*, *J* = 9.8)	70.7
13	1.98–2.00 (*m*)	49.1	2.06–2.10 (*m*)	48.2	2.02[a])	48.2
14		51.3		51.7		51.6
15	0.99[a]), 1.57[a])	30.7	1.71–1.73, 1.16–1.20 (2*m*)	31.5	1.56–1.59, 1.01–1.06 (2*m*)	31.3
16	1.28–1.34 (*m*), 1.82[a])	26.6	1.80–1.86, 1.37–1.40 (2*m*)	26.9	1.78–1.82 (*m*), 1.37[a])	26.8
17	2.57[a])	51.5	2.30–2.34 (*m*)	54.8	2.29[a])	54.7
18	1.01 (*s*)	17.6	1.23 (*s*)	17.6	1.12 (*s*)	17.3
19	1.09 (*s*)	17.4	1.04 (*s*)	17.4	0.96 (*s*)	17.6
20		83.4		72.9		72.9
21	1.64 (*s*)	22.3	1.41 (*s*)	27.0	1.39 (*s*)	27.0
22	1.75–1.77, 2.33–2.37 (2*m*)	36.2	2.05[a]), 1.69[a])	35.8	2.04[a]), 1.68–1.72 (*m*)	35.8
23	2.37–2.40 (*m*), 2.58[a])	23.1	2.58–2.64, 2.25–2.30 (2*m*)	22.9	2.58–2.62 (*m*), 2.26[a])	23.0
24	5.31 (*t*, *J* = 6.2)	126.0	5.31 (*t*, *J* = 7.2)	126.2	5.30 (*t*, *J* = 7.1)	126.3
25		131.0		130.8		130.7
26	1.60 (*s*)	25.8	1.61 (*s*)	25.8	1.60 (*s*)	25.8
27	1.64 (*s*)	17.9	1.65 (*s*)	17.9	1.63 (*s*)	17.6
28	1.97 (*s*)	31.9	2.01 (*s*)	31.5	2.03 (*s*)	31.9
29	1.44 (*s*)	16.5	1.55 (*s*)	16.5	1.39 (*s*)	16.9
30	0.97 (*s*)	17.4	0.91(*s*)	16.9	0.87 (*s*)	16.9

Table (cont.)

Position	**1**		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
	20-Glc		6-Glc		6-Xyl	
1′	5.11 (*d*, *J* = 7.8)	98.0	5.06 (*d*, *J* = 7.8)	106.2	5.09 (*d*, *J* = 6.2)	104.2
2′	3.89 (*t*, *J* = 8.4)	74.8	4.09[a])	75.3	4.40[a])	80.0
3′	4.35 – 4.37 (*m*)	79.3	4.22 (*t*, *J* = 8.9)	79.2	4.34[a])	77.6
4′	4.18 – 4.21 (*m*)	71.6	4.01 (*t*, *J* = 9.3)	71.5	4.20[a])	70.9
5′	4.03[a])	76.9	4.09[a])	75.1	4.41[a]), 3.73 (*dd*, *J* = 11.4, 8.9)	66.2
6′	4.75 (*dd*, *J* = 11.5, 1.3), 4.30[a])	70.3	5.11 (*dd*, *J* = 11.7, 1.6), 4.78 (*dd*, *J* = 11.7, 6.7)	65.1		
	6′-Glc		6′-But-2-enoyl		6′-Xyl	
1″	5.01 (*d*, *J* = 7.7)	105.5		166.5	5.65 (*d*, *J* = 7.4)	104.9
2″	3.96 (*t*, *J* = 8.1)	75.1	6.05 (*dq*, *J* = 15.6, 1.4)	123.1	4.15[a])	75.6
3″	4.14[a])	78.3	7.09 (*dq*, *J* = 15.8, 6.8)	144.8	4.15[a])	78.7
4″	4.15[a])	71.5	1.74 (*dd*, *J* = 6.9, 1.7)	17.6	4.22[a])	71.2
5″	4.03[a])	77.0			4.31[a]), 3.64 (*t*, *J* = 10.7)	67.3
6″	4.29[a]), 4.80 (*dd*, *J* = 11.5, 2.0)	69.9				
	6″-Xyl					
1‴	4.94 (*d*, *J* = 7.5)	105.9				
2‴	4.01[a])	74.8				
3‴	4.11[a])	78.1				
4‴	4.02[a])	71.1				
5‴	3.63 – 3.67, 4.30 – 4.32 (2*m*)	67.1				

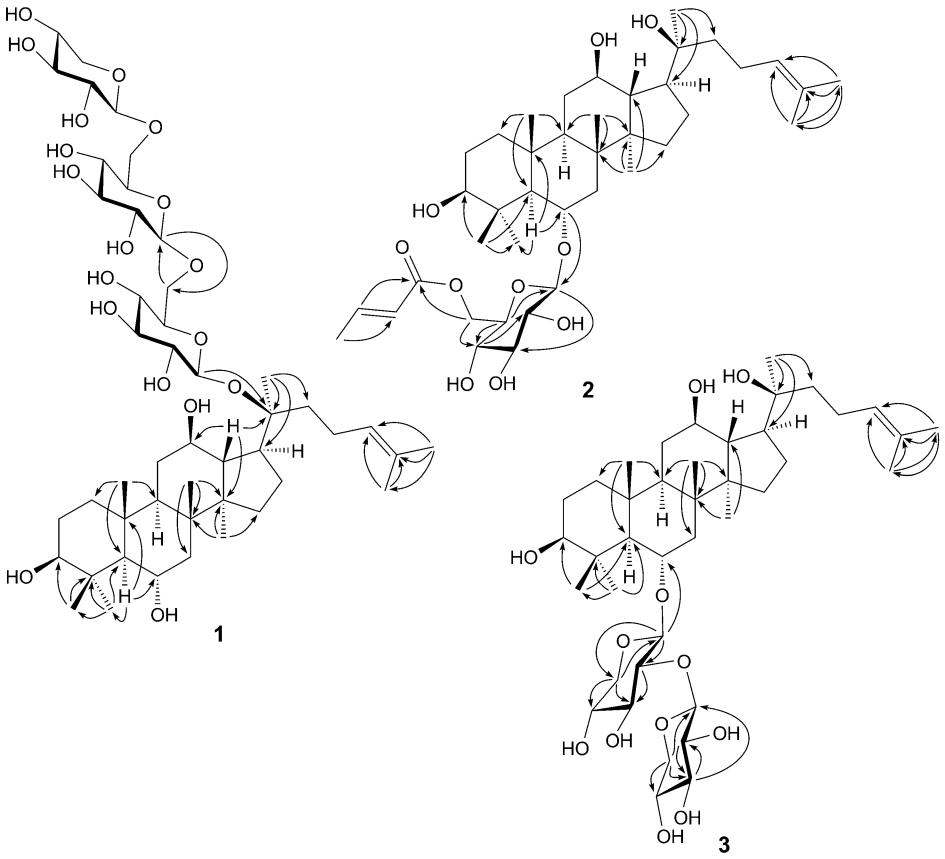


Fig. 3. *Key HMBCs of* **1**–**3**

signals were displayed, including those of two olefinic C-atom signals of C(24) (δ(C) 126.2) and C(25) (δ(C) 130.8). The signals of C(5) and C(6) were shifted downfield to δ(C) 61.4 and 80.0, respectively. In addition, the ^{1}H-NMR spectrum showed an anomeric H-atom signal at δ(H) 5.06 (d, $J = 7.8$, H–C(1′)), which showed HSQC to the C-atom signal at δ(C) 106.2 (C(1′)). Based on the coupling constant of the anomeric H-atom, the sugar substituent was identified as β-configurated, and acid hydrolysis of **2** revealed the presence of a glucose moiety, identified by GC/MS analysis [25]. The above data suggested that compound **2** was also a protopanaxatriol-type ginsenoside, and that the sugar unit was at C(6). The location of the sugar unit at C(6) (δ(C) 80.0) was established by the HMBC experiment (*Fig. 3*). The anomeric H-atom at δ(H) 5.06 (d, $J = 7.8$, H–C(1′)) was correlated through a three-bond coupling with C(6) (δ(C) 80.0), and the H–C(6) signal (δ(H) 4.38) correlated, in turn, with the anomeric C-atom signal at δ(C) 106.2 (C(1′)). The presence of a butenoyl group was confirmed on the basis of HSQC and HMBC data (HMBCs from H–C(3″) (δ(H) 7.09) to C(1″) (δ(C) 166.5), and from H–C(4″) (δ(H) 1.74) to C(2″) (δ(C) 123.1) and C(3″) (δ(C) 144.8)).

The HMBCs from H–C(6′) (δ(H) 5.11) to C(1″) (δ(C) 166.5), coupled with the C-atom signal of C(6′) downfield-shifted (δ(C) 63.0 to 65.1) by comparing it with that of ginsenoside Rh_1, revealed that the butenoyl group was at C(6′) of the glucose unit. The relative configurations at the ring junctions were confirmed by NOESY spectrum, which have revealed the correlations from H–C(3) (δ(H) 3.50) to H–C(5) (δ(H) 1.41 – 1.43) and Me(28) (δ(H) 2.01), from H–C(6) (δ(H) 4.38) to Me(18) (δ(H) 1.23) and Me(19) (δ(H) 1.04), and from H–C(12) (δ(H) 3.90 – 3.94) to H–C(9) (δ(H) 1.57) and Me(30) (δ(H) 0.91) (*Fig. 4*). The NOE correlations from H–C(17) (δ(H) 2.30 – 2.34) to H–C(12) (δ(H) 3.90 – 3.94), Me(21) (δ(H) 1.41), and Me(30) (δ(H) 0.91) suggested that the configuration at C(20) should be (*S*). Furthermore, the HMBCs from Me(26) (δ(H) 1.61) and Me(27) (δ(H) 1.65) to C(24) (δ(C) 126.2), from H–C(24) (δ(H) 5.31) to C(26) (δ(C) 25.8) and C(27) (δ(C) 17.9) confirmed that the C=C bond is located in the side chain. The ^{1}H- and ^{13}C-NMR assignments for **2** were accomplished unambiguously based on HSQC and HMBC data. Thus, the structure of **2** was determined as (20*S*)-(6-*O*-[(*E*)-but-2-enoyl-(1 → 6)-β-D-glucopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol.

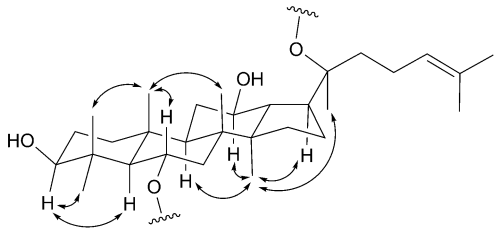


Fig. 4. *Selected NOESY correlations of* **1** – **3**

Compound **3** was isolated as a white amorphous powder. Its molecular formula was determined as $C_{40}H_{68}O_{12}$ by HR-ESI-MS (*m*/*z* 763.4605 $[M+Na]^+$, $C_{40}H_{68}NaO_{12}^+$; calc.763.4608) and NMR data. Comparing the ^{1}H- and ^{13}C-NMR data of **3** with those of **1** and **2**, all these three compounds turned out to possess the same aglycone moiety. In the ^{1}H-NMR ((D_5)pyridine) spectrum of **3**, signals of eight Me groups at δ(H) 0.87, 0.96, 1.12, 1.39 (2×), 1.60, 1.63, 2.03 (each *s*, Me(30), Me(19), Me(18), Me(21), Me(29), Me(26), Me(27), Me(28), resp.) and of an olefinic H-atom at δ(H) 5.30 (*t*, *J* = 7.1, H–C(24)) were displayed, and in the ^{13}C-NMR spectrum of **3**, 40 C-atom signals were detected, including those of two olefinic C-atom signals of C(24) (δ(C) 126.3) and C(25) (δ(C) 130.7). The signals of C(5) and C(6) were shifted downfield to δ(C) 61.2, and 78.8, respectively. In addition, the ^{1}H-NMR spectrum exhibited two anomeric H-atom signals at δ(H) 5.09 (*d*, *J* = 6.2, H–C(1′)) and 5.65 (*d*, *J* = 7.4, H–C(1″), which showed HSQCs to C-atom signal at δ(C) 104.2 (C(1′)) and 104.9 (C(1″)). Based on the coupling constant of the anomeric H-atom, the sugar substituent was identified as β-configurated, and acid hydrolysis of **3** revealed the presence of a xylcose moiety, identified by GC/MS analysis [25]. All these data suggested that compound **3** was also a protopanaxatriol-type ginsenoside, and the sugar unit was at C(6). The location of the sugar unit at C(6) (δ(C) 78.8) was established by the HMBC experiment (*Fig. 3*). The signal of the anomeric H-atom at δ(H) 5.09 (*d*, *J* = 6.2, H–C(1′)) correlated through a

three-bond coupling with that of C(6) (δ(C) 78.8), and the H–C(6) signal (δ(H) 4.32) correlated, in turn, with that of the anomeric C-atom at δ(C) 104.2 (C(1′)). The relative configurations at the ring junctions were confirmed by NOESY spectrum, which exhibited correlations from H–C(3) (δ(H) 3.45–4.49) to H–C(5) (δ(H) 1.38) and Me(28) (δ(H) 2.03), from H–C(6) (δ(H) 4.32) to Me(18) (δ(H) 1.12) and Me(19) (δ(H) 0.96), and from H–C(12) (δ(H) 3.90) to H–C(9) (δ(H) 1.52) and Me(30) (δ(H) 0.87) (*Fig. 4*). The NOE correlation from H–C(17) (δ(H) 2.29) to H–C(12) (δ(H) 3.90), Me(21) (δ(H) 1.39), and Me(30) (δ(H) 0.87), suggested that the configuration at C(20) should be (*S*). Furthermore, the HMBCs from Me(26) (δ(H) 1.60) and Me(27) (δ(H) 1.63) to C(24) (δ(C) 126.3), from H–C(24) (δ(H) 5.30) to C(26) (δ(C) 25.8) and C(27) (δ(C) 17.6) confirmed that the C=C bond was located in the side train. The ^{1}H- and ^{13}C-NMR assignments for **3** were achieved unambiguously based on HSQC and HMBC data. Thus, the structure of **3** was determined as (20*S*)-6-*O*-[β-D-xylopyranosyl-(1 → 2)-β-D-xylopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol.

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Experimental Part

General. Column chromatography (CC): silica gel *G* (SiO_2; 100–200 and 200–300 mesh, *Qingdao Sea Chemical Factory*, P. R. China), *D101* macroporous resin (*Cangzhou Bon Adsorber Technology Co., Ltd.*, P. R. China), and *Sephadex LH-20* (*Amersham Biosciences*, Germany). Medium-pressure liquid-chromatography (MPLC): *MCI* gel (*CHP20P*, 75–150 μm; *Mitsubishi Chemical Corporation*, Japan) and reversed-phase C_{18} silica gel (40–63 μm; *Merck*, Germany). TLC: precoated silica gel *G* plates (*Qingdao Sea Chemical Factory*, P. R. China); visualization with 10% H_2SO_4 in alcohol, followed by heating. MPLC: *Eyela Ceramic VSP 3050* pump, *Eyela* glass column (300 × 30 mm). Prep. HPLC: *Shimadzu LC-6AD* pump, *Shimadzu SPD-20A* UV detector, *YMC ODS-A* (20 × 250 mm, 10 μm). M.p.: *X-4* micro-melting-point apparatus (*Shanghai*, P. R. China); uncorrected. IR Spectra: *PerkinElmer Spectrum One* FT-IR spectrometer. NMR Spectra: *Bruker ARX-600* spectrometer in (D_5)pyridine with TMS as an internal standard. ESI-MS: *Agilent 1100-LC/MS DTrap SL*. HR-ESI-MS: *Waters API QSTAR Pular-1* mass spectrometer and a *Waters Synapt G2* MS mass spectrometer. GC/MS: *Agilent 7000B Triple Quad GC/MS-7890* GC system.

Plant Material. The roots of *Panax notoginseng* were purchased in *Yi Xin Pharmaceutical Co. Ltd.* (Nanning, Guangxi) in October, 2011. The sample was authenticated by TCM-Pharmacist *Jia-Fu Wei* from Guangxi Zhuang Autonomous Region Food and Drug Administration. A voucher specimen No. SQ20111019 was deposited with the Laboratory of Natural Products of the College of Pharmacy, Guangxi Medical University.

Extraction and Isolation. Dried roots (8.9 kg) of *Panax notoginseng* were extracted with tenfold 80% EtOH under reflux, and *ca.* 1,800 g of extract were obtained. The extract was suspended in H_2O and then partitioned with CH_2Cl_2 and BuOH successively.

The BuOH (1517 g) extract was subjected to CC (*D101* macroporous resin; H_2O/EtOH 100:0 → 0:100): *Frs. B1–B5*. *Fr. B3* (256 g) was subjected to CC (*D101* macroporous resin; H_2O/EtOH 90:10 → 70:30): *Frs. B31–B32*. *Fr. B32* (56 g) was subjected to CC (SiO_2; CH_2Cl_2/MeOH 100:1 → 0:100): *Frs. B321–B327. Fr. B326* (10 g) was recrystallized from MeOH/H_2O to yield **11** (5536 mg). The mother soln. from *Fr. B326* was subjected to MPLC (RP C_{18} silica gel; H_2O/MeOH 100:0 → 0:100): *Frs. B3261–B3266*. *Fr. B3264* (0.21 g) and *Fr. B3265* (0.53 g) were submitted to prep. HPLC (MeOH/

H_2O 70:30) to afford **1** (51 mg), **24** (141 mg), and **16** (145 mg). *Fr. B325* (37 g) was subjected to MPLC (RP C_{18} silica gel; H_2O/MeOH 100: 0 → 0:100): *Frs. B3251 – B3255*. *Fr. B3251* (0.2 g) was submitted to prep. HPLC (MeOH/H_2O 50:50) to furnish **12** (17 mg). *Fr. B3254* (1.4 g) was purified by CC (*Sephadex LH-20*; $CHCl_3$/MeOH, 1:1) and prep. HPLC (MeOH/H_2O 53:47) to afford **4** (79 mg), **11** (105 mg), and **14** (53 mg). *Fr. B327* (8.8 g) was subjected to MPLC (RP C_{18} silica gel; H_2O/MeOH 100: 0 → 0:100): *Frs. B3271 – B3277*. *Fr. B3275* (7.7 g) was separated by CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1:1) and prep. HPLC (MeOH/H_2O 62:38) to give **19** (5536 mg), **20** (87 mg), **21** (422 mg), **22** (320 mg), and **23** (68 mg). *Fr. B5* (150 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH/H_2O 100:0:0 → 6:4:0.4): *Frs. B51 – B55*. *Fr. B55* (80 g) was purified by CC (SiO_2; $CHCl_3$/MeOH 10:1 → 1:1): *Frs. B521 – B524*. *Fr. B523* (8.1 g) was separated by MPLC (*MCI* gel; H_2O/MeOH, 30:70 → 0:100) and prep. HPLC (MeOH/H_2O 70:30) to yield **6** (129 mg) and **10** (30 mg). *Fr. B524* (2.1 g) was separated by MPLC (RP C_{18} silica gel; H_2O/MeOH 70: 30 → 0:100), MPLC (*MCI* gel; H_2O/MeOH 100:0 → 0:100), and prep. HPLC (MeOH/H_2O 50:50) to furnish **3** (9 mg), **5** (100 mg), **8** (100 mg), and **9** (50 mg). *Fr. B54* (100 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 8:2 → 7:3): *Frs. B541 – B543*. *Fr. B543* (92 g) was re-subjected to CC (SiO_2; AcOEt/EtOH/H_2O 5:1:0 → 6:3:0.3) to afford **17** (200 mg) and **18** (531 mg).

The CH_2Cl_2 extract (72 g) was subjected to CC (SiO_2; CH_2Cl_2/MeOH 1:0 → 5:1): *Frs. C1 – C7*. *Fr. C6* (8.2 g) was separated by CC (SiO_2; $CHCl_3$/MeOH 20:1 → 5:1): *Frs. C61 – C65*. *Fr. C64* (2.8 g) was submitted to MPLC (*MCI* gel; H_2O/MeOH, 50:50 → 0:100): *Frs. C641 – C644*. *Fr. C641* (1.1 g) was subjected to MPLC (RP C_{18} silica gel; H_2O/MeOH 100: 0 → 0:100), and prep. HPLC (MeOH/H_2O 60:40) to give **2** (15 mg), **7** (54 mg), **15** (15 mg), and **16** (135 mg).

*(20*S*)-20-*O*-[β-*D*-Xylopyranosyl-(1 → 6)-β-*D*-glucopyranosyl-(1 → 6)-β-*D*-glucopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol* (= *(3β,6α,12β)-3,6,12-Trihydroxydammar-24-en-20-yl* O-*β*-D-*Xylopyranosyl-(1 → 6)*-O-*β*-D-*glucopyranosyl-(1 → 6)*-*β*-D-*glucopyranoside*; **1**). White amorphous power (MeOH). M.p. 187–188°. IR (KBr): 3399, 2927, 1638, 1384, 1042. ^{1}H- and ^{13}C-NMR: see the *Table*. HR-ESI-MS (pos.): 955.5229 ($[M+Na]^+$, $C_{47}H_{80}NaO_{18}^+$; calc. 955.5242).

*(20*S*)-6-*O*-[(*E*)-But-2-enoyl-(1 → 6)-β-*D*-glucopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol* (= *(3β,6α,12β)-3,12,20-Trihydroxydammar-24-en-6-yl 6*-O-*[(2*E*)-1-Oxobut-2-en-1-yl]-β-*D*-glucopyranoside*; **2**). White amorphous power (MeOH). M.p. 159–160°. IR (KBr): 3399, 2933, 2962, 1712, 1655, 1384, 1029. ^{1}H- and ^{13}C-NMR: see the *Table*. HR-ESI-MS (pos.): 1413.9362 ($[2M+H]^+$, $C_{80}H_{133}O_{20}^+$; calc. 1413.9390).

*(20*S*)-6-*O*-[β-*D*-Xylopyranosyl-(1 → 2)-β-*D*-xylopyranosyl]dammar-24-ene-3β,6α,12β,20-tetrol* (= *(3β,6α,12β)-3,12,20-Trihydroxydammar-24-en-6-yl 2*-O-*β*-D-*Xylopyranosyl-β*-D-*xylopyranoside*; **3**). White amorphous power (MeOH). M.p. 171–172°. IR (KBr): 3391, 2932, 1642, 1384, 1033. ^{1}H- and ^{13}C-NMR: see the *Table*. HR-ESI-MS (pos.): 763.4605 ($[M+Na]^+$, $C_{40}H_{68}NaO_{12}^+$; calc. 763.4608).

Acid Hydrolysis of **1**–**3**. Each compound (1.5 mg) was hydrolyzed with 1.5 ml of 1M HCl at 100° for 4 h. The mixture was extracted with $CHCl_3$ (3×), and the aq. residue was evaporated under reduced pressure. Then, 1 ml of pyridine and 2 mg of $NH_2OH \cdot HCl$ were added to the residue, and the mixture was heated at 90° for 1 h. After cooling, Ac_2O (0.5 ml) was added, and the mixture was heated at 90° for 1 h. The mixtures were evaporated under reduced pressure, and the resulting aldononitrile peracetates were analyzed by GC/MS using standard aldononitrile peracetates as reference samples.

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