New Dammarane Monodesmosides from the Acidic Deglycosylation of Notoginseng-Leaf Saponins

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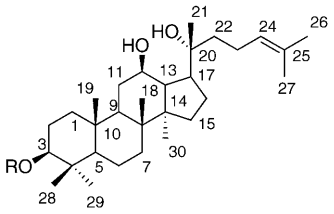
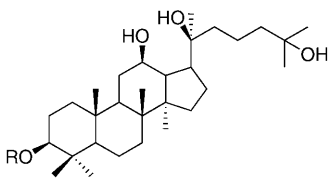
Three new dammarane monodesmosides, named notoginsenosides Ft_1 (**1**), Ft_2 (**2**), and Ft_3 (**3**), together with three known ginsenosides, were obtained from a mild acidic hydrolysis of the saponins from notoginseng (*Panax notoginseng* (BURK.) F. H. CHEN) leaves. Their structures were elucidated to be (3*β*,12*β*,20*R*)-12,20-dihydroxydammar-24-en-3-yl *O*-*β*-D-xylopyranosyl-(1 → 2)-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranoside (**1**), (3*β*,12*β*)-12,20,25-trihydroxydammaran-3-yl *O*-*β*-D-xylopyranosyl-(1 → 2)-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranoside (**2**), and (3*β*,12*β*,24*ξ*)-12,20,24-trihydroxydammar-25-en-3-yl *O*-*β*-D-xylopyranosyl-(1 → 2)-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranoside (**3**), by means of spectroscopic evidences. The known ginsenosides Rh_2 and Rg_3 **4**–**6** were obtained as the major products from this acidic deglycosylation.

Introduction. – Ginsenosides as an important class of dammarane-type tetracyclic triterpenoid saponins have been isolated from the plants of *Panax* genus (Araliaceae) and recognized as the pharmaceutically active principles of Chinese ginseng or Korean ginseng (*P. ginseng* MEYER), American ginseng (*P. quenquefolium* L.) and notoginseng (*P. notoginseng* (BURK.) F. H. CHEN). Many reports showed that ginsenosides have a wide spectrum of medicinal effects, *e.g.*, tonic, immunomodulatory, anticarcinogenic, antimutagenic and cancer preventing [1], antiamnestic and antiaging [2][3], and radioprotective effects [4], and are active in cardiovascular-disease prevention and treatment [5].

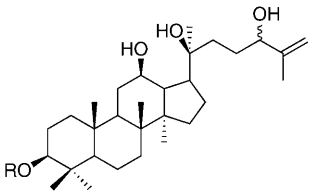
Notoginseng (Sanchi-Ginseng or Tienchi-Ginseng) is an indigenous herb of the southern Yunnan province, China. Its root as a famous traditional Chinese medicine has been used in China since a long time ago for the treatment of cardiovascular diseases, inflammation, and internal and external bleeding due to injury, while the extract of leaves is used as a medicine for treating insomnia [6]. Extensive chemical studies of this plant led to the isolation of a series of dammarane type protopanaxadiol and protopanaxatriol saponins [7]. The chemical composition of notoginseng-leaf saponins is distinctly different from those of the root saponins. In the leaves, protopanaxadiol saponins are the main constituents, such as ginsenosides Rb_3, Rb_1, and Rd, (20*S*)-and (20*R*)-ginsenoside Rg_3, Rh_2 and F_2, notoginsenosides Fa, Fc, and Fe, and gypenosides IX, XIII, and XVII, whereas the content of protopanaxatriol saponins, *e.g.* ginsenosides Rg_1 and Re, and notoginsenoside R_1, which are the major saponins in the roots, is very low in the leaves [7a][8]. To enhance the molecular diversity of ginsenosides, which concomitantly enhances the chances to find new biologically active substances, our pre-



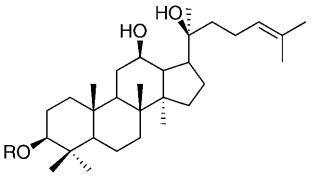
1 R = Xyl(1→2)Glc(1→2)Glc
6 R = Glc(1→2)Glc



2 R = Xyl(1→2)Glc(1→2)Glc



3 R = Xyl(1→2)Glc(1→2)Glc



4 R = Glc
5 R = Glc(1→2)Glc

vious work dealt with several new dammarane glycosides obtained by mild acidic hydrolysis of notoginseng-root saponins [9][10].

As part of our continuing search for the molecular diversity of dammarane glycosides from *Panax* plants, we now describe the isolation and structural elucidation of three new dammarane monodesmosides, notoginsenosides Ft_1, Ft_2, and Ft_3 (**1**–**3**), and the three known ginsenosides (**4**–**6**) from an acid hydrolysate of the notoginseng-leaf saponins.

Results and Discussion. – The notoginseng-leaf saponins were treated under mild acidic conditions (EtOH/AcOH 1:1), and the hydrolysate was repeatedly chromatographed (*Diaion HP-20*, silica gel, and reversed-phase silica gel) to afford the three new dammarane monodesmosides **1**–**3** and the three known saponins **4**–**6**. The known compounds were identified as (20*S*)-ginsenoside Rh_2 (**4**) [11], (20*S*)-ginsenoside Rg_3 (**5**), and (20*R*)-ginsenoside Rg_3 (**6**) [12] by direct comparison with authentic samples and by comparison of their spectroscopic data with reported ones[1]).

Notoginsenoside Ft_1 (**1**) was obtained as white amorphous powder, and had a molecular formula $C_{47}H_{80}O_{17}$, derived from the negative HR-FAB-MS (*m*/*z* 915.5283 ($[M-H]^-$)). Comparison of the NMR data (*Tables 1* and *2*) with those of (20*R*)-ginsenoside Rg_3 (**6**) [12] and the 2D-NMR data allow to elucidate the structure of compound **1** as (3*β*,12*β*,20*R*)-12,20-dihydroxydammar-24-en-3-yl *O*-*β*-D-xylopyranosyl-(1 → 2)-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranoside.

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[1]) The systematic names of **4**–**6** are: (3*β*,12*β*)-12,20-dihydroxydammar-24-en-3-yl *β*-D-glucopyranoside (**4**), (3*β*,12*β*)-12,20-dihydroxydammar-24-en-3-yl *O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranoside (**5**), and (3*β*,12*β*,20*R*)-12,20-dihydroxydammar-24-en-3-yl *O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranoside (**6**).

Table 1. *^{1}H-NMR Data of Compounds* **1**–**3**. At 500 MHz in C_5D_5N; δ in ppm, J in Hz.

	1	**2**	**3**
H_α–C(1)	0.70–0.84 (*m*)	0.71–0.84 (*m*)	0.70–0.83 (*m*)
H_β–C(1)	1.49–1.57 (*m*)	1.45–1.55 (*m*)	1.46–1.56 (*m*)
H_α–C(2)	2.19 (*dd*, *J*=4.2, 13.8)	2.19 (*dd*, *J*=3.4, 12.3)	2.18 (*dd*, *J*=3.4, 12.3)
H_β–C(2)	1.76–1.87 (*m*)	1.75–1.87 (*m*)	1.77–1.89 (*m*)
H–C(3)	3.29 (*dd*, *J*=4.2, 11.5)	3.27 (*dd*, *J*=4.3, 11.5)	3.28 (*dd*, *J*=4.3, 11.5)
H–C(5)	0.62–0.75 (*m*)	0.63–0.77 (*m*)	0.61–0.55 (*m*)
H_α–C(6)	1.44–1.54 (*m*)	1.44–1.56 (*m*)	1.45–1.55 (*m*)
H_β–C(6)	1.30–1.42 (*m*)	1.30–1.40 (*m*)	1.30–1.42 (*m*)
H_α–C(7)	1.19–1.30 (*m*)	1.18–1.27 (*m*)	1.13–1.27 (*m*)
H_β–C(7)	1.42–1.56 (*m*)	1.40–1.52 (*m*)	1.38–1.54 (*m*)
H–C(9)	1.36–1.45 (*m*)	1.35–1.44 (*m*)	1.35–1.45 (*m*)
H_α–C(11)	1.95–2.05 (*m*)	1.95–2.04 (*m*)	1.94–2.04 (*m*)
H_β–C(11)	1.46–1.59 (*m*)	1.46–1.57 (*m*)	1.45–1.59 (*m*)
H–C(12)	3.85–3.96 (*m*)	3.85–3.95 (*m*)	3.86– 3.95 (*m*)
H–C(13)	1.96–2.06 (*m*)	1.95–2.06 (*m*)	1.95–2.08 (*m*)
H_α–C(15)	1.00–1.09 (*m*)	1.01–1.11 (*m*)	1.00–1.10 (*m*)
H_β–C(15)	1.50–1.63 (*m*)	1.47–1.61 (*m*)	1.50–1.63 (*m*)
H_α–C(16)	1.88–2.01 (*m*)	1.86–1.99 (*m*)	1.83–1.96 (*m*)
H_β–C(16)	1.31–1.42 (*m*)	1.35–1.47 (*m*)	1.35–1.47 (*m*)
H–C(17)	2.40 (*dd*, *J*=6.9, 10.2)	2.30–2.41 (*m*)	2.29–2.40 (*m*)
Me(18)	1.00 (*s*)	0.99 (*s*)	0.96 (*s*)
Me(19)	0.80 (*s*)	0.79 (*s*)	0.80 (*s*)
Me(21)	1.42 (*s*)	1.40 (*s*)	1.42 (*s*)
CH_2(22)	1.69–1.80 (*m*),	1.91–2.06 (*m*),	1.53–1.67 (*m*),
	1.65–1.77 (*m*)	1.49–1.60 (*m*)	1.40–1.52 (*m*)
CH_2(23)	2.50–2.61 (*m*),	2.04–2.16 (*m*),	1.76–1.90 (*m*),
	2.41–2.53 (*m*)	1.87–1.99 (*m*)	1.65–1.75 (*m*)
H–C(24) or CH_2(24)	5.32 (*t*, *J*=7.2)	1.54–1.69 (*m*)	4.43 (*t*, *J*=6.0)
		2.31–2.46 (*m*)	
Me(26) or CH_2(26)	1.69 (*s*)	1.40 (*s*)	5.19–5.32 (*m*),
			5.21–5.35 (*m*)
Me(27)	1.65 (*s*)	1.39 (*s*)	1.91 (s)
Me(28)	1.29 (*s*)	1.29 (*s*)	1.28 (*s*)
Me(29)	1.11 (*s*)	1.08 (*s*)	1.09 (*s*)
Me(30)	0.98 (*s*)	0.93 (*s*)	0.95 (*s*)
3-*O*-Glc:			
H–C(1′)	4.93 (*d*, *J*=7.5)	4.90 (*d*, *J*=7.3)	4.90 (*d*, *J*=7.3)
H–C(2′)	4.22 (*t*, *J*=7.7)	4.22 (*t*, *J*=7.7)	4.22 (*t*, *J*=7.7)
H–C(3′)	4.20 (*t*, *J*=7.7)	4.19 (*t*, *J*=7.7)	4.19 (*t*, *J*=7.7)
H–C(4′)	4.14 (*t*, *J*=9.5)	4.11 (*t*, *J*=9.5)	4.11 (*t*, *J*=9.5)
H–C(5′)	3.83–3.94 (*m*)	3.83–3.92 (*m*)	3.82–3.91 (*m*)
CH_2(6′)	4.55 (*dd*, *J*=2.5, 11.2),	4.53 (*dd*, *J*=2.6, 11.8),	4.53 (*dd*, *J*=2.6, 11.8),
	4.33 (*dd*, *J*=3.0, 11.2)	4.33 (*dd*, *J*=3.0, 11.2)	4.33 (*dd*, *J*=3.0, 11.2)
Glc:			
H–C(1″)	5.51 (*d*, *J*=7.7)	5.54 (*d*, *J*=7.7)	5.53 (*d*, *J*=7.7)
H–C(2″)	4.24 (*t*, *J*=7.7)	4.21 (*dd*, *J*=7.7, 9.2)	4.22 (*dd*, *J*=7.7, 9.2)
H–C(3″)	4.28 (*t*, *J*=7.7)	4.28 (*t*, *J*=7.7)	4.28 (*t*, *J*=7.7)
H–C(4″)	4.33 (*t*, *J*=7.7)	4.30 (*t*, *J*=7.7)	4.30 (*t*, *J*=7.7)
H–C(5″)	3.89–3.99 (*m*)	3.86–3.96 (*m*)	3.86–3.97 (*m*)

Table 1 (cont.)

	1	**2**	**3**
CH_2(6″)	4.49 (*dd*, *J* = 3.3, 11.6), 4.46 (*dd*, *J* = 4.2, 11.6)	4.47 (*dd*, *J* = 2.9, 11.5), 4.43 (*dd*, *J* = 3.7, 11.5)	4.47 (*dd*, *J* = 2.9, 11.5), 4.43 (*dd*, *J* = 3.7, 11.5)
Xyl:			
H–C(l‴)	5.71 (*d*, *J* = 7.5)	5.72 (*d*, *J* = 7.5)	5.72 (*d*, *J* = 7.5)
H–C(2‴)	4.08–4.16 (*m*)	4.07–4.16 (*m*)	4.08–4.15 (*m*)
H–C(3‴)	4.21–4.34 (*m*)	4.21–4.35 (*m*)	4.21–4.35 (*m*)
H–C(4‴)	4.16–4.26 (*m*)	4.14–4.25 (*m*)	4.15–4.25 (*m*)
CH_2(5‴)	4.27–4.40 (*m*), 3.63 (*t*, *J* = 10.4)	4.30–4.42 (*m*), 3.63 (*t*, *J* = 10.4)	4.30–4.41 (*m*), 3.63 (*t*, *J* = 10.4)

Table 2. *^{13}C-NMR Data of Compounds* **1**–**3**. At 125 MHz in C_5D_5N; δ in ppm.

	1	**2**	**3**		**1**	**2**	**3**
C(1)	39.2 (*t*)	39.2 (*t*)	39.3 (*t*)	C(26)	25.9 (*q*)	30.0 (*q*)	111.1 (*t*)
C(2)	26.7 (*t*)	26.8 (*t*)	26.8 (*t*)	C(27)	17.7 (*q*)	30.2 (*q*)	17.2 (*q*)
C(3)	89.0 (*d*)	89.0 (*d*)	89.2 (*d*)	C(28)	28.2 (*q*)	28.2 (*q*)	28.2 (*q*)
C(4)	39.8 (*s*)	39.8 (*s*)	39.9 (*s*)	C(29)	16.7 (*q*)	16.7 (*q*)	16.8 (*q*)
C(5)	56.4 (*d*)	56.4 (*d*)	56.6 (*d*)	C(30)	17.4 (*q*)	17.4 (*q*)	17.2 (*q*)
C(6)	18.5 (*t*)	18.5 (*t*)	18.5 (*t*)	3-*O*-Glc:			
C(7)	35.2 (*t*)	35.2 (*t*)	35.3 (*t*)	C(1′)	104.8 (*d*)	104.8 (*d*)	104.8 (*d*)
C(8)	40.1 (*s*)	40.0 (*s*)	40.2 (*s*)	C(2′)	83.0 (*d*)	83.0 (*d*)	82.9 (*d*)
C(9)	50.4 (*d*)	49.3 (*d*)	49.7 (*d*)	C(3′)	78.0 (*d*)	78.0 (*d*)	78.0 (*d*)
C(10)	37.0 (*s*)	37.0 (*s*)	37.1 (*s*)	C(4′)	71.9 (*d*)	71.9 (*d*)	71.9 (*d*)
C(11)	32.2 (*t*)	32.2 (*t*)	32.2 (*t*)	C(5′)	77.8 (*d*)	77.8 (*d*)	77.7 (*d*)
C(12)	71.2 (*d*)	71.2 (*d*)	71.3 (*d*)	C(6′)	63.0 (*t*)	63.0 (*t*)	63.1 (*t*)
C(13)	49.2 (*d*)	48.7 (*d*)	48.7 (*d*)	Glc:			
C(14)	51.8 (*s*)	51.7 (*s*)	51.8 (*s*)	C(1″)	103.2 (*d*)	103.2 (*d*)	103.3 (*d*)
C(15)	31.5 (*t*)	31.5 (*t*)	31.5 (*t*)	C(2″)	84.6 (*d*)	84.6 (*d*)	84.7 (*d*)
C(16)	26.8 (*t*)	26.8 (*t*)	26.8 (*t*)	C(3″)	78.3 (*d*)	78.3 (*d*)	78.3 (*d*)
C(17)	50.7 (*s*)	54.8 (*s*)	54.9 (*s*)	C(4″)	70.9 (*d*)	70.9 (*d*)	71.0 (*d*)
C(18)	15.9 (*q*)	15.9 (*q*)	16.0 (*q*)	C(5″)	77.8 (*d*)	77.8 (*d*)	77.7 (*d*)
C(19)	16.4 (*q*)	16.4 (*q*)	16.5 (*q*)	C(6″)	63.0 (*t*)	63.0 (*t*)	63.1 (*t*)
C(20)	73.1 (*s*)	73.5 (*s*)	73.3 (*s*)	Xyl:			
C(21)	22.8 (*q*)	28.2 (*q*)	27.5 (*q*)	C(1‴)	106.5 (*d*)	106.5 (*d*)	106.5 (*d*)
C(22)	43.2 (*t*)	36.7 (*t*)	32.3 (*t*)	C(2‴)	76.0 (*d*)	75.9 (*d*)	75.9 (*d*)
C(23)	22.7 (*t*)	19.3 (*t*)	30.7 (*t*)	C(3‴)	78.7 (*d*)	78.7 (*d*)	78.7 (*d*)
C(24)	126.1 (*d*)	45.7 (*t*)	76.1 (*d*)	C(4‴)	0.8 (*d*)	70.8 (*d*)	70.8 (*d*)
C(25)	130.8 (*s*)	70.0 (*s*)	150.0 (*s*)	C(5‴)	67.5 (*t*)	67.5 (*t*)	67.4 (*t*)

The negative FAB-MS of **1** exhibited fragment ion peaks at *m*/*z* 783 ($[M-H-132(\text{pentosyl})]^-$ and 621 ($[M-H-132-162(\text{hexosyl})]^-$), suggesting the presence of pentosyl and hexosyl units in **1** and a pentosyl unit as the terminal sugar moiety. The ^{1}H-NMR spectra (*Table 1*) showed the presence of three anomeric protons at δ 4.93 (*d*, *J* = 7.5 Hz, H–C(1′)), 5.51 (*d*, *J* = 7.7 Hz, H–C(1″)), and 5.71 (*d*, *J* = 7.5 Hz, H–C(1‴)). Combining with the ^{13}C-NMR data (*Table 2*), this suggested the presence of two glucopyranosyl and one xylopyranosyl units in **1**. The large coupling constants of the anomeric protons was compatible with the β-configuration for all sugar moieties [13]. Comparison of the NMR data of **1** with those of **6** [12] indicated that **1** had one more xylopyranosyl unit than **6**. The linkage of the sugar moiety in **1** was unambiguously established by 2D-NMR experiments. In the HMBC spectrum of **1**, the

long-range correlations from H–C(1′) (δ 4.93) to C(3) (δ 89.0), H–C(1″) (δ 5.51) to C(2′) (δ 83.0), and H–C(1‴) (δ 5.71) to C(2″) (δ 84.6), revealed the linkage sequence of sugar units. Moreover, the ROESY correlations of H–C(1‴) with H–C(1″), H–C(2″), and H–C(3″), of H–C(1″) with H–C(1′), H–C(2′), and H–C(3′), and of H–C(1′) with H–C(2), H–C(3), Me(28), and Me(29) confirmed the structure of the trisaccharide linkage.

Compound **2** possessed a molecular formula $C_{47}H_{82}O_{18}$, as deduced from the negative HR-FAB-MS (*m/z* 933.5408 ($[M-H]^-$)). On the basis of the spectral data (*Tables 1* and *2*) and comparison with compound **1**, the structure of notoginsenoside Ft_2 (**2**) was established to be (3*β*,12*β*)-12,20,25-trihydroxydammaran-3-yl *O*-*β*-D-xylopyranosyl-(1 → 2)-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranoside.

The ^{1}H- and ^{13}C-NMR data of **2** closely resembled those of **1**, except for the obvious differences concerning C(24) (δ 45.7) and C(25) (δ 70.0) (*Table 2*). In addition, the ^{1}H-NMR spectrum (*Table 1*) showed an upfield shift of the Me(26) and Me(27) signals to δ 1.40 and 1.39. These observations indicated the presence of a tertiary OH group at C(25), which was further confirmed by the ^{1}H,^{13}C-HMBC correlations of Me(26) and Me(27) with C(24). The *S*-configuration at C(20) was determined by comparison of the chemical shifts of C(17), C(21), C(22), and C(23) with literature data [13][14].

The molecular formula of notoginsenoside Ft_3 (**3**) was determined to be $C_{47}H_{80}O_{18}$ on the basis of the HR-FAB-MS (*m/z* 931.5318 ($[M-H]^-$)). Comparison of the ^{13}C-NMR data of **3** (*Table 2*) with those of compound **1** and of the reported majoroside F_1 [15] and bipinnatifidusoside F_1 [16] determined the structure of compound **3** to be (3*β*,12*β*,24*ξ*)-12,20,24-trihydroxydammar-25-en-3-yl *O*-*β*-D-xylopyranosyl-(1 → 2)-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranoside.

The NMR data (*Tables 1* and *2*) of **3** including the sugar residues, were closely related to those of **1** and **2**, except for signals arising from the side chain of the aglycone. Instead of the olefinic methine C-atom of **1** at δ 126.1 (C(24)), an olefinic methylene C-atom at δ 111.1 was displayed in the ^{13}C-NMR spectrum of **3**. Moreover, the quaternary olefinic C-atom of **1** at δ 130.8 (C(25)) was downfield shifted to δ 150.0 in **3**. These observations suggested that the C=C bond between C(24) and C(25) of **1** was shifted to the terminus of the side chain of **3** (C(25)=CH_2(26)). In addition, a chemical shift at δ 76.1 suggested the presence of an OH group at the side chain. Comparison of the ^{13}C-NMR data of **3** with those of majoroside F_1 from *P. japonicus* var. *major* [15] and bipinnatifidusoside F_1 from *P. japonicus* var. *bipinnatifidus* [16] confirmed that the C=C bond of **3** was located between C(25) and C(26) and the OH group at C(24). These features were substantiated by the intense ^{1}H,^{13}C-HMBC correlations of H–C(24) with C(22) and C(26), and of Me(27) with C(24) and C(26). Other key HMBC correlations corroborated the structure of **3**.

Thus, the deglycosylation reaction of notoginseng-leaf saponins by a careful mild acidic hydrolysis led to the formation of several new analogous of monodesmosides and enhanced the molecular diversity of ginsenosides. Moreover, ginsenosides Rg_3 **5** and **6** and (20*S*)-ginsenoside Rh_2 (**4**), three well known promising anticancer-active products with very low content in ginseng, were obtained as the major products in this hydrolysis. These results demonstrate that the controlled hydrolysis of the crude saponins of ginseng and of related plants increases the molecular diversity of this specific natural-product family, which may provide further exploring opportunities or lead to compounds for drug applications.

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Experimental Part

General. The crude saponins from notoginseng (*Panax notoginseng* (BURK.) F. H. CHEN) leaves were purchased from *Yuxi Weihe Pharm. Co*., Yunnan province, the People's Republic of China. Column chromatography (CC): silica gel (160–200 mesh; *Qingdao Marine Chemical Products Industry Factory*, China), *Rp-8* or *Rp-18* silica gel (40–60 μm; *Merck*), and highly porous polymer resin *MCI* gel *HP-20* (*Mitsubishi Chemical Co.*). TLC: silica gel *G* precoated plates (*Qingdao Haiyan Chemical Co.*) with $CHCl_3$/MeOH/H_2O 7:3:0.5, and *Rp-8-F254S* precoated plates (*Merck*, Art.15682); detection by spraying with 10% H_2SO_4 soln. followed by heating. M.p.: *XRC-1* instrument, produced by the Sichuan University, China. 1D- and 2D-NMR Spectra: *Bruker-DRX*-500 MHz instrument, δ in ppm rel. to $SiMe_4$ as internal standard, *J* in Hz. MS: *VG-Autospect-3000* spectrometer; in *m*/*z*.

Acid Hydrolysis and Product Isolation. A soln. of the crude notoginseng-leaf saponins (250 g) in EtOH/AcOH 1:1 (2 l) was heated at 60° for 6 h. The mixture was neutralized with 10% aq. NaOH soln. and then concentrated *i.v.* to remove EtOH. The aq. residue was then subjected to CC (*Diaion HP-20*, H_2O and MeOH). The MeOH fraction (200 g) was separated by CC (silica gel, $CHCl_3$/MeOH/H_2O 10:2.5:0.3): 7 fractions. Each fraction was further purified by repeated CC (silica gel, *Rp-8*, and *Rp-18*): **4** (4.5 g), **5** (3.8 g), **6** (4.3 g), **1** (32 mg), **2** (12 mg) and **3** (13 mg).

*(3β,12β,20*R*)-12,20-Dihydroxydammar-24-en-3-yl* O-*β*-D-*Xylopyranosyl-(1 → 2)*-O-*β*-D-*glucopyranosyl-(1 → 2)*-*β*-D-*glucopyranoside (=Notoginsenoside Ft$_1$*; **1**): White amorphous powder. M.p. 238–240°. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (neg.): 915 ($[M-H]^-$), 783 ($[M-132$(xylosyl)$-H]^-$), 621 ($[M-132$(xylosyl)-162(glucosyl)$-H]^-$). HR-FAB-MS: 915.5283 ($[M-H]^-$, $C_{47}H_{79}O_{17}^-$; calc. 915.5323)

*(3β,12β)-12,20,25-Trihydroxydammaran-3-yl O-*β*-*D*-Xylopyranosyl-(1 → 2)*-O-*β*-D-*glucopyranosyl-(1 → 2)*-*β*-D-*glucopyranoside (=Notoginsenoside Ft$_2$*; **2**): White amorphous powder. M.p. 208–210°. ^{1}H- and ^{13}C- NMR: *Tables 1* and *2*. FAB-MS (neg.): 933 ($[M-H]^-$), 801 ($[M-132$(xylosyl)$-H]^-$), 639 ($[M-132$(xylosyl)-162(glucosyl)$-H]^-$). HR-FAB-MS: 933.5408 ($[M-H]^-$, $C_{47}H_{81}O_{18}^-$; calc. 933.5428).

(3β,12β,24ξ)-12,20,24-Trihydroxydammar-25-en-3-yl O-*β*-D-*Xylopyranosyl-(1 → 2)*-O-*β*-D-*glucopyranosyl-(1 → 2)*-*β*-D-*glucopyranoside* (=*Notoginsenoside Ft$_3$*; **3**): White amorphous powder. M.p. 223–225°. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. FAB-MS (neg.): 931 ($[M-H]^-$), 799 ($[M-132$(xylosyl)$-H]^-$), 637 ($[M-132$(xylosyl)-162(glucosyl)$-H]^-$). HR-FAB-MS: 931.5318 ($[M-H]^-$, $C_{47}H_{79}O_{18}^-$; calc. 931.5272).

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