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Dammarane-Type Glycosides from Steamed Notoginseng

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Notoginseng, the root of *Panax notoginseng* (Burk.) F. H. Chen (Araliaceae), is a Chinese traditional medicine, which is used in both raw and processed forms due to their different pharmacological activities. Detailed chemical investigation on steamed notoginseng led to the isolation of 27 dammarane-type triterpenoids (**1**–**27**), including 4 new glycosides, namely, notoginsenosides ST-1−ST-3 and ST-5 (**1**–**4**), in addition to 3 other known compounds. Of the new compounds, **1**–**3** possess new aglycones. Their structures were elucidated on the basis of detailed analyses of their 1D and 2D NMR spectra and chemical reactions. The known compounds, koryoginsenoside-R_1 (**19**), yesanchinoside D (**20**), 6″-*O*-acetylginsenoside Rg_3 (**24**), and 3β,6α,12β-trihydroxydammar-20(21),24-diene (**25**), were isolated from notoginseng for the first time.

KEYWORDS: Steamed notoginseng; *Panax notoginseng*; dammarane; notoginsenosides ST-1−ST-3 and ST-5

INTRODUCTION

Notoginseng, the root of *Panax notoginseng* (Burk.) F. H. Chen (Araliaceae), a traditional Chinese medicinal herb, is mainly cultivated in Yunnan province of China. Traditionally, notoginseng has been used in two forms, raw and processed. The former is mainly used for injuries from falls and removing blood stasis, whereas the latter is used as a tonic to promote blood circulation (*1*). It is well-known that dammarane-type triterpenoidal saponins are the main bioactive constituents of notoginseng, from which more than 30 saponins have been isolated (*2*). In the 1980s, we compared the saponin compositions in processed notoginseng to those in the raw one and found that the contents of bisdesmosides (such as ginsenosides Rg_1, Rb_1, Rd, Re, and notoginsenoside R1) in the processed form were lower, whereas the monodesmosides (such as ginsenosides Rg_2, Rg_3, and notoginsenoside R2) increased (*3*). In recent years, Lau et al. (*4, 5*) reported that the concentrations of less polar saponins, for examaple, ginsenosides 20(*S*)-Rh_1, 20(*R*)-Rh_1, Rk_3, Rh_4, 20(*S*)-Rg_3, 20(*R*)-Rg_3, Rk_1, and Rg_5, increased in steamed notoginseng, by HPLC analyses. However, no systematic phytochemical studies on the steamed notoginseng were reported. As a part of our continuing studies on the chemical constituents of *Panax* medicinal plants, the present study was undertaken to isolate and structurally elucidate new dammarane glycosides, together with known dammarane-type triterpenoids and other types of known compounds from the steamed notoginseng.

MATERIALS AND METHODS

Material. Air-dried notoginseng was obtained from Wenshan County, Yunnan Province, China, in May 2006. The raw materials were crushed into small grains and then steamed at 120 °C for 12 h directly, without mixing with water, to give the steamed notoginseng, which was used for extraction and isolation in this study.

Apparatus. Optical rotations were performed on a P-1020 polarimeter (JASCO, Tokyo, Japan). IR spectra were measured on a Bruker Tensor 27 spectrometer with KBr pellets. ^{1}H and ^{13}C NMR, ^{1}H−^{1}H COSY, HMQC, HMBC, ROSEY, and TOCSY spectra were recorded in C_5D_5N with Bruker AM-400 and DRX-500 spectrometers. Coupling constants are expressed in hertz, and chemical shifts are given on a δ (parts per million) scale with TMS as an internal standard. FAB-MS were recorded on an AutoSpec 3000 spectrometer (VG, Manchester, U.K.) with glycerol as the matrix, in *m*/*z*. HRESI-MS were recorded on an API Qstar Pulsa LC/TOF spectrometer. Melting points (mp) were determined on an *XRC-I* melting point apparatus, produced by Sichuan University, China (uncorrected).

Column chromatography (CC) was performed with Diaion 101 resin (Shandong Lukang Pharmaceutical Co., Ltd., China), silica gel (200–300 mesh) (Qingdao Marine Chemical and Industrial Factory, China), MCI-gel CHP20P (75–100 μm) (Mitsubishi Chemical Co., Ltd., Japan), and Rp-8 or Rp-18 gel (40–60 μm) (Merck, Darmstadt, Germany). TLC was performed with silica gel H precoated plates (Qingdao Marine Chemical and Industrial Factory, China) with $CHCl_3$/MeOH/H_2O (75:25:3; 80:20:2; 85:15:1; or 90:10:1, v/v) and $CHCl_3$/MeOH (90:10 to

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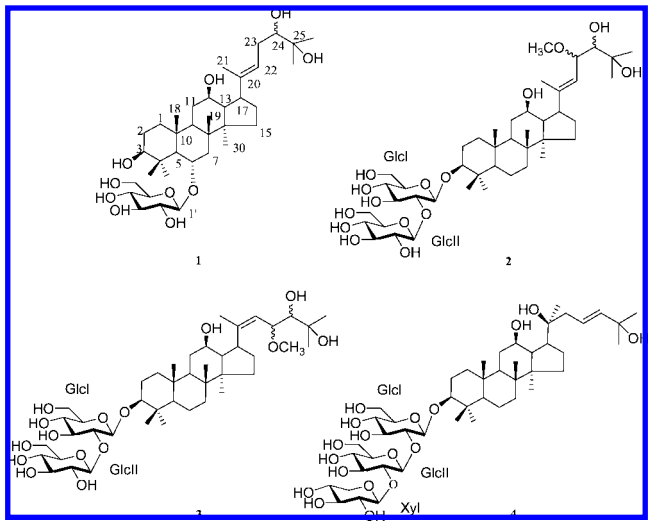

Figure 1. New compounds **1**−**4** isolated from the steamed notoginseng.

25:1, v/v) and Rp-8 or Rp-18 precoated plates (Merck) with MeOH/H_2O (60:40 to 100:0, v/v). Spots were detected by spraying with 10% H_2SO_4 in EtOH followed by heating.

Extraction and Isolation. The air-dried steamed notoginseng (4.7 kg) was powdered and extracted with ethanol four times. The ethanolic extract was concentrated under reduced pressure to afford a residue (778 g). The residue was dissolved in H_2O and passed through a Diaion 101 column (90 × 8.5 cm) two times, eluting with H_2O and MeOH, successively. The methanol eluates were combined and concentrated under reduced pressure to give a residue (440 g), which was further subjected to silica gel column chromatography eluted with ($CHCl_3$:MeOH:H_2O, 85:15:1) to afford nine fractions (1–9). Fraction 1 (13 g) was repeatedly chromatographed over silica gel ($CHCl_3$/MeOH/H_2O), Rp-8, Rp-18, and MCI-gel CHP20P columns (MeOH/H_2O) to afford **5** (252 mg) and **6** (89 mg). In a similar way, compounds **25** (30 mg), **26** (23 mg), **27** (32 mg), **28** (666 mg), **29** (157 mg), and **30**(191 mg) from fraction 3 (21 g), compounds **1** (14 mg), **2** (51 mg), **3** (41 mg), **7** (25 mg), **8** (6 mg), **17** (33 mg), **18** (83 mg), **19** (10 mg), **20** (15 mg), **21** (20 mg), **22** (48 mg) and **24** (16 mg) from fraction 5 (60 g), compounds **9** (151 mg), **10** (23 mg), **11** (71 mg), **16** (20 mg), and **23** (238 mg) from fraction 7 (38 g), and compounds **4** (21 mg), **12** (114 mg), **13** (720 mg), **14** (1076 mg), and **15** (36 mg) from fraction 9 (40 g) were obtained, respectively, through repeated column chromatography (**Figures 1** and **2**).

Notoginsenoside ST-1 [3β,6α,12β,24,25-pentahydroxydammar-20(22)(*E*)-ene-6-*O*-β-D-glucopyranoside] (**1**) was obtained as a white amorphous powder: mp 168–171 °C; $[\alpha]_D^{26}$ +29.1° (*c* 0.249, MeOH); IR (KBr), ν_{max} (cm^{-1}) 3424, 2961, 2931, 2876, 1637, 1462, 1384, 1156, 1075, 1031, 928, 890; FAB-MS (negative ion mode), *m/z* 653 $[M - H]^-$, 491 $[M - 162(glucosyl) - H]^-$; HRESIMS (negative ion mode), *m/z* 653.4270 $[M - H]^-$, (calcd for 653.4264, $C_{36}H_{61}O_{10}$); ^1H and ^{13}C NMR data, see **Tables 1**−**3**.

Notoginsenoside ST-2 [3β,12β,24,25-tetrahydroxy-23-methoxydammar-20(22)(*E*)-ene-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside] (**2**) was obtained as a white amorphous powder: mp 172–177 °C; $[\alpha]_D^{26}$ −9.4° (*c* 0.264, MeOH); IR (KBr), ν_{max} (cm^{-1}) 3417, 2944, 2877, 1640, 1549, 1465, 1452, 1388, 1370, 1077, 1033, 978; FAB-MS (negative ion mode), *m/z* 831 $[M + 1]^-$; HRESIMS (negative ion mode), *m/z* 829.4942 $[M - H]^-$ (calcd for 829.4949, $C_{43}H_{73}O_{15}$); ^1H and ^{13}C NMR data, see **Tables 1**−**3**.

Notoginsenoside ST-3 [3β,12β,24,25-tetrahydroxy-23-methoxydammar-20(22)(*Z*)-ene-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside] (**3**) was obtained as a white amorphous powder: mp 171–175 °C; $[\alpha]_D^{26}$ +20.3° (*c* 0.254, MeOH); IR (KBr), ν_{max} (cm^{-1}) 3418, 2944, 2877, 1640, 1549, 1465, 1453, 1389, 1372, 1161, 1078, 1038, 978; FAB-MS (negative ion mode), *m/z* 830 $[M]^-$, 668 $[M - 162(glucosyl)]^-$; HRESIMS (negative ion mode), *m/z* 829.4955 $[M - H]^-$ (calcd for 829.4949, $C_{43}H_{73}O_{15}$); ^1H and ^{13}C NMR data, see **Tables 1**−**3**.

Notoginsenoside ST-5 [3β,12β,20(*S*),25-tetrahydroxydammar-23-ene-3-*O*-β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside] (**4**) was obtained as a white amorphous powder: mp 193–196 °C; $[\alpha]_D^{26}$ +2.3° (*c* 0.257, MeOH); IR (KBr), ν_{max} (cm^{-1}) 3422, 2940, 2878, 1639, 1461, 1375, 1077, 1043, 896; FAB-MS (negative ion mode), *m/z* 932 $[M]^-$, 800 $[M - 132(xylosyl)]^-$, 476 $[M - 132$ (xylosyl) − 162(glucosyl) − 162(glucosyl)$]^-$; HRESIMS (negative ion mode), *m/z* 931.5241 $[M - H]^-$ (calcd for 931.5266, $C_{47}H_{79}O_{18}$); ^1H and ^{13}C NMR data, see **Tables 1**−**3**.

Acid Hydrolysis of Compounds 1–4. Compounds **1**−**3** (each 5 mg) were hydrolyzed with 2 M HCl/dioxane (1:1, 4 mL) under reflux for 8 h, respectively. The reaction mixture was partitioned between H_2O and $CHCl_3$ (2 mL × 3). The aqueous layer was neutralized with 2 M NaOH and then dried to give a monosaccharide mixture. A solution of the sugar mixture in pyridine (2 mL) was added to L-cysteine methyl ester hydrochloride (about 1.5 mg) and kept at 60 °C for 1 h. Then trimethylsilylimidazole (about 1.5 mL) was added to the reaction mixture and kept at 60 °C for 30 min. The mixture was subjected to GC analysis, run on a Shimadzu GC-14C gas chromatograph equipped with an H_2 flame ionization detector. The column was a 30 m × 0.32 mm i.d. 30QC2/AC-5 quartz capillary column with the following conditions: column temperature, 180−280 °C; programmed increase, 3 °C/min; carrier gas, N_2 (1 mL/min); injector and detector temperature, 250 °C; injection volume, 4 μL; and split ratio, 1/50. The configuration of the sugar moiety was determined by comparing the retention time with the derivatives of the authentic samples. The retention times of D-/L-glucose were 21.115/21.565 min. The configuration of the sugar moiety from compounds **1**−**3** was D-glucose.

Compound **4** (8 mg) was treated as described for compounds **1**−**3** to give the monosaccharide mixture, which was detected by GC analysis running on an Agilent Technologies HP5890 gas chromatograph. The retention times of D-/L-glucose and D-/L-xylose were 19.715/20.159 and 14.606/15.256 min, respectively. The configuration of the sugar moiety from compound **4** was D-glucose and D-xylose.

RESULTS AND DISCUSSION

The ethanolic extracts of the steamed notoginseng were chromatographed repeatedly over Diaion 101 resin, silica gel, Rp-8, Rp-18, and MCI-gel CHP20P column to yield 4 new dammarane-type glycosides, notoginsenosides ST-1−ST-3 (**1–3**) and ST-5 (**4**), and 26 known compounds (**5–30**).

The known compounds were identified as ginsenosides Rh_4 (**5**) (*6*), Rk_3 (**6**) (*6*), Rg_5 (**7**) (*6*), Rk_1 (**8**) (*6*), Rg_1 (**9**) (*7*), Rg_2 (**10**) (*7*), Rf (**11**) (*8*), Re (**12**) (*7*), Rb_1 (**13**) (*9*), and Rd (**14**) (*9*), notoginsenosides R1 (**15**) and R2 (**16**) (*8*), sanchinoside-B_1 (**17**) (*10*), 25-hydroxy-20(*R*)-ginsenoside Rh_1 (**18**) (*7*), koryoginsenoside-R_1 (**19**) (*11*), yesanchinoside D (**20**) (*12*), 20(*S*)-ginsenoside Rh_1 (**21**) (*7*), 20(*R*)-ginsenoside Rh_1 (**22**) (*7*), 20(*R*/*S*)-ginsenoside Rg_3 (**23**) (*13*),6″-*O*-acetylginsenoside Rg_3 (**24**) (*14, 15*), 3β,6α,12β-trihydroxydammar-20(21),24-diene (**25**) (*16, 17*), 20(*S*)-protopanaxtriol (**26**) (*18*), 20(*R*)-protopanaxtriol (**27**) (*18*), panaxytriol (**28**) (*19, 20*), (*Z*,*Z*)-9,12-octadecadienoic acid 2-hydroxy-1,3-propanedinyl ester (**29**) (*21*), and 5-hydroxymethyl-2-furancarboxaldehyde (**30**) (*22*), respectively, on the basis of FAB-MS, NMR spectra data, and comparison with those reported in the literature. Among them, glycosides **19**, **20**, and **24**, as well as the aglycone **25**, were isolated from *P. notoginseng* for the first time.

Compound **1** was obtained as a white amorphous powder. Its molecular formula $C_{36}H_{62}O_{10}$ was determined by negative high-resolution electrospray ionization (HRESI) mass spectrometry and confirmed by DEPT spectra. The IR spectrum showing strong absorbances at 3424, 1637, 1384, 1075, 1031, 928, and 890 cm^{-1} suggested the presence of hydroxyl groups and a double bond in **1**. The fragment ion peaks at 653 $[M - H]^-$ and 491 $[M - H - 162(hexosyl)]^-$ in fast atom bombardment (FAB)-MS, and the anomeric proton and

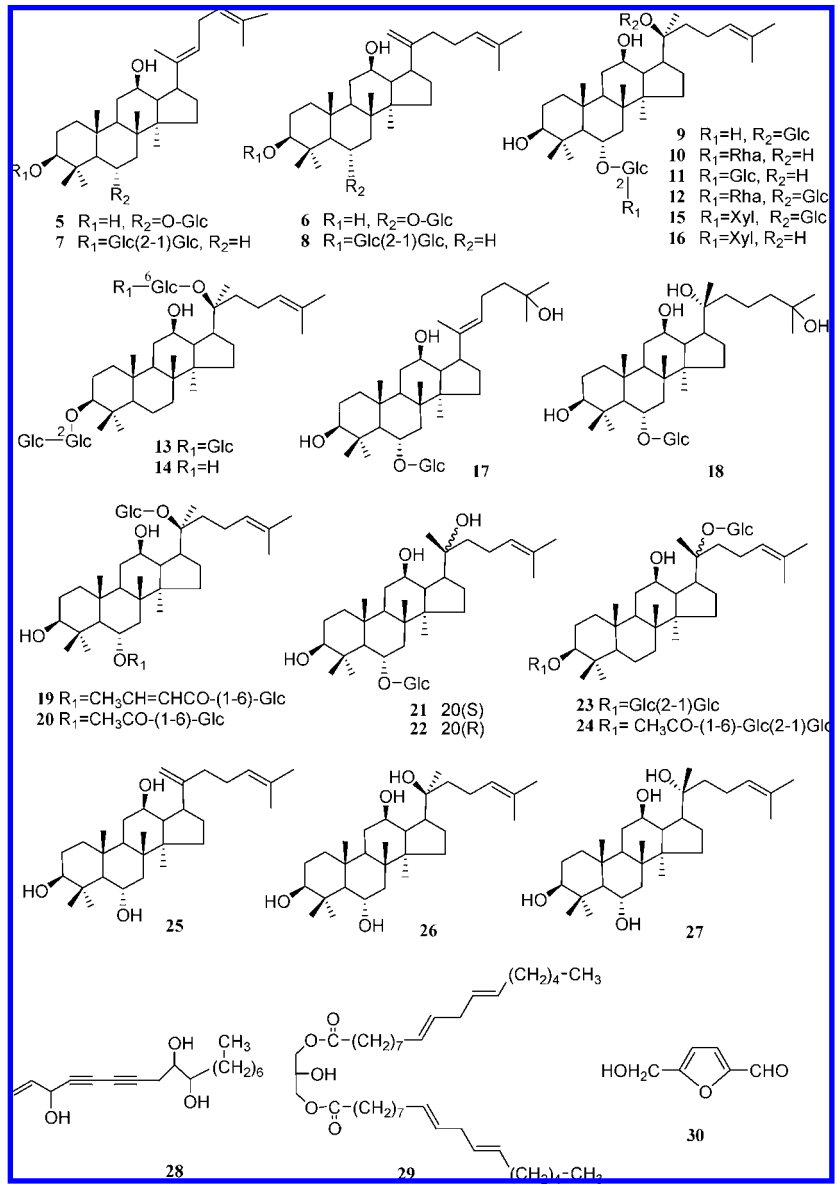

Figure 2. Known compounds **5**−**30** from the steamed notoginseng.

carbon signals at δ_H 5.03 (d, J = 8.0 Hz) and δ_C 106.1, respectively, in ^{1}H and ^{13}C NMR suggested the presence of a β-hexosyl unit in **1**. Acid hydrolysis of **1** gave D-glucose as the sugar component, indicating **1** was a β-D-glycoside. The NMR data of **1** were similar to those of sanchinoside-B_1 (**17**), except that **1** had one more hydroxyl group located on the side chain of the aglycone. The structure of **1** was further elucidated by 2D NMR experiments. In the proton–proton homonuclear shift correlated spectroscopy (^{1}H−^{1}H COSY) spectrum, the methylene signal at δ_H 2.58 (m, H-23) was found to be coupled with both an olefinic proton at δ_H 5.74 (t, J = 7.0 Hz, H-22) and an oxygenated methine at δ_H 3.80 (m, H-24). The heteronuclear multiple-bond correlation (HMBC) spectrum exhibited the following long-range correlation signals: δ_H 2.82 (H-17) with δ_C 141.8 (C-20), 13.1 (C-21) and 123.9 (C-22); δ_H 1.83 (H-21) with δ_C 51.3 (C-17), C-20 and C-22; δ_H 5.74 (H-22) with δ_C 31.2 (C-23), C-17, and C-21; δ_H 2.58 (H-23) with δ_C 79.0 (C-24), C-20, and C-22; δ_H 3.80 (H-24) with δ_C 72.3 (C-25) and C-22; and δ_H 1.51 (H-26) and 1.49 (H-27) with C-24 and C-25, respectively. These data confirmed that the additional hydroxyl group was located at C-24. In addition, the HMBC correlation between δ_H 5.03 (H-1′) and δ_C 80.1 (C-6) revealed that the β-D-glucosyl unit was located at C-6 of the aglycone.

In the rotating frame Overhauser effect spectroscopy (ROSEY) spectrum of **1**, the methyl proton at δ_H 1.83 (s, H-21) was correlated with δ_H 2.58 (H-23), but not with the olefinic proton at δ_H 5.74 (H-22). This observation indicated that the C-20(22) double bond was of the *E* form. The chemical shift of the C-21 methyl group (δ_C 13.1) was similar to those of ginsenoside Rh_4 (*23*), sanchinoside-B_1 (*10*), and notoginsenoside T_1 (*24*). Thus, the structure of notoginsenoside ST-1 (**1**) was determined as 3β,6α,12β,24,25-pentahydroxydammar-20(22)(*E*)-ene-6-*O*-β-D-glucopyranoside.

The molecular formula of compound **2** was established as $C_{43}H_{74}O_{15}$ by the quasimolecular ion peak in the negative HRESIMS. Its NMR features were similar to that of ginsenoside Rg_5 (**7**) (*6*), except for the side chain of the aglycone. Compared with compound **7**, compound **2** had one fewer double bond, but one more methoxyl and two more hydroxyl groups (δ_H 3.32, δ_C 55.1, 72.3, and 80.7) on the side chain. In the ^{1}H−^{1}H COSY spectrum of **2**, the oxygen-bearing methine proton at δ_H 4.31

Table 1. ^{13}C NMR Spectroscopic Data of Compounds **1**−**4** (δ, in C_5D_5N)

no.	1	2	3	4
1	39.5	39.3	39.3	39.2
2	28.0	26.8	26.8	26.8
3	78.6	88.9	89.0	89.0
4	40.4	39.8	39.8	39.8
5	61.5	56.4	56.4	56.5
6	80.1	18.5	18.5	18.5
7	45.4	35.4	35.4	35.2
8	41.4	40.3	40.3	40.2
9	50.5	50.7	51.0	50.5
10	39.8	37.1	37.0	37.0
11	32.7	32.3	33.2	32.2
12	72.5	71.9	72.2	71.2
13	50.3	51.0	52.0	49.0
14	50.7	50.9	51.1	51.8
15	32.5	32.7	32.7	31.3
16	27.7	28.6	30.0	26.8
17	51.3	51.4	50.1	54.2
18	16.9	16.5	16.5	16.5
19	17.4	15.9	15.9	15.9
20	141.8	143.5	145.3	73.4
21	13.1	13.3	15.5	27.7
22	123.9	123.5	123.2	40.1
23	31.2	79.5	78.2	123.9
24	79.0	80.7	80.7	142.0
25	72.3	72.3	72.5	69.9
26	26.6	29.4	28.5	30.8
27	26.0	24.8	26.1	30.8
28	31.8	28.2	28.2	28.2
29	16.4	16.7	16.6	16.7
30	17.7	17.0	17.1	17.1
OCH_3		55.1	55.4	
Glcl-1′	106.1	105.2	105.2	104.8
Glcl-2′	75.5	83.4	83.4	83.0
Glcl-3′	79.7	78.0	78.0	78.7
Glcl-4′	71.9	71.6	71.6	71.1
Glcl-5′	78.2	78.4	78.4	78.3
Glcl-6′	63.1	62.7	62.9	63.0
GlclI-1″		106.1	106.1	103.2
GlclI-2″		77.2	77.2	84.6
GlclI-3″		78.2	78.2	78.0
GlclI-4″		71.6	71.6	71.9
GlclI-5″		78.4	78.4	77.8
GlclI-6″		62.8	62.7	63.0
Xyl-1‴				106.5
Xyl-2‴				76.0
Xyl-3‴				77.8
Xyl-4‴				70.8
Xyl-5‴				67.5

(H-23) was coupled with both olefinic proton at δ_H 5.68 (H-22) and another oxygen-bearing methine proton at δ_H 3.85 (H-24). Moreover, the HMBC correlations of H-17 (δ_H 2.83) with C-20 (δ_C 143.5), C-21 (δ_C 13.3), and C-22 (δ_C 123.5); H-21 (δ_H 1.91) with C-17 (δ_C 51.4), C-20 and C-22; H-22 with C-17, C-21, and C-24 (δ_C 80.7); H-23 with C-20 and C-24; H-24 (δ_H 3.85) with C-22, C-23 (δ_C 79.5), C-25 (δ_C 72.3), C-26 (δ_C 29.4), and C-27 (δ_C 24.8); H-26 (δ_H 1.60) and H-27 (δ_H 1.45) with C-24 and C-25, and the methoxyl protons (δ_H 3.32) with C-23 revealed the structure of the side chain in **2**.

The *E* form of the C-20(22) double bond was determined by the ROSEY spectrum, in which correlation of the methyl proton at δ_H 1.91 (H-21) with the methoxyl proton at δ_H 3.32 was observed; however, there was no correlation between H-21 and the olefinic proton at δ_H 5.68 (H-22). The sugar sequence and location were confirmed by the HMBC correlations of one anomeric proton at δ_H 4.90 (d, J = 7.5 Hz, H-1′) with C-3 (δ_C 88.9) of the aglycone and another anomeric proton at δ_H 5.35 (d, J = 7.7 Hz, H-1″) with C-2′ (δ_C 83.4) of the inner glucosyl unit. On the basis of the above evidence, compound **2** was elucidated to be 3β,12β,24,25-tetrahydroxy-23-methoxydammar-20(22)(*E*)-ene-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside and named notoginsenoside ST-2.

Table 2. ^1H NMR Spectroscopic Data for the Aglycone Moieties of Compounds **1–4** [δ (*J*, Hertz), in C_5D_5N]

no.	1	2	3	4
1	1.70 m	1.50 m	1.45 m	1.48 m
	1.03 m	0.74 m	0.72 m	0.78 m
2	1.93 m	2.18 m	2.17 m	2.19 m
	1.85 m	1.81 m	1.80 m	1.86 m
3	3.53 dd	3.26 m	3.28 dd	3.30 m
	(4.5, 11.5)		(4, 11.5)	
5	1.44 m	0.66 m	0.66 m	0.69 m
6	4.43 m	1.49 m	1.47 m	1.49 m
		1.36 m	1.34 m	1.38 m
7	2.53 m	1.46 m	1.45 m	1.48 m
	1.97 m	1.22 m	1.21 m	1.25 m
9	1.57 m	1.36 m	1.35 m	1.40 m
11	2.04 m	1.91 m	1.91 m	2.03 m
	1.46 m	1.41 m	1.36 m	1.49 m
12	3.94 m	3.83 m	3.87 m	3.90 m
13	1.99 m	1.97 m	2.09 m	2.06 m
15	1.72 m	1.67 m	1.69 m	1.60 m
	1.16 m	1.10 m	1.08 m	1.04 m
16	1.86 m	1.94 m	2.01 m	1.91 m
	1.42 m	1.57 m	1.52 m	1.47 m
17	2.82 m	2.83 m	2.77 m	2.36 m
18	0.82 s	0.79 s	0.75 s	0.80 s
19	1.22 s	1.01 s	0.97 s	1.02 s
21	1.83 s	1.91 s	2.08 s	1.43 s
22	5.74 t (7.0)	5.68 d (9.8)	5.80 d (9.7)	2.78 m
				2.49 m
23	2.58 m	4.31 m	4.48 m	6.31 m
24	3.80 m	3.85 d (6.5)	3.77 d (4.9)	6.02 d (15.5)
26	1.51 s	1.60 s	1.56 s	1.55 s
27	1.49 s	1.45s	1.52 s	1.54 s
28	2.07 s	1.26 s	1.27 s	1.28 s
29	1.61 s	1.08 s	1.08 s	1.11 s
30	1.03 s	0.91 s	0.93 s	0.94 s
OCH_3		3.32 s	3.41 s	

Table 3. ^1H NMR Spectroscopic Data for the Sugar Moieties of Compounds **1–4** [δ (*J*, Hertz), in C_5D_5N]

no.	1	2	3	4
Glcl-1′	5.03d (8.0)	4.90 d (7.5)	4.92 d (7.5)	4.93 d (7.5)
Glcl-2′	4.10 t (8.5)	4.20 m	4.23 m	4.14 m
Glcl-3′	4.27 m	4.21 m	4.24 m	4.35 m
Glcl-4′	4.22 m	4.11 m	4.13 m	4.09 m
Glcl-5′	3.96 m	3.90 m	3.92 m	3.95 m
Glcl-6′	4.53 dd (2.5, 11.5)	4.53 m	4.56 m	4.57 br.d (10)
	4.37 dd (5.5, 12.0)	4.32 m	4.35 m	4.34 m
GlclI-1″		5.35 d (7.7)	5.37 d (7.6)	5.53 d (7.5)
GlclI-2″		4.08 m	4.11 m	4.18 m
GlclI-3″		4.28 m	4.31 m	4.28 m
GlclI-4″		4.30 m	4.31 m	4.18 m
GlclI-5″		3.90 m	3.92 m	3.87 m
GlclI-6″		4.46 m,	4.48 m,	4.50 m br.d
		4.44 m	4.45 m	
Xyl-1‴				5.39 d (6.5)
Xyl-2‴				4.09 m
Xyl-3‴				4.32 m
Xyl-4‴				4.14 m
Xyl-5‴				4.34 m
				3.68 m

Compound **3** showed the same molecular formula, $C_{43}H_{74}O_{15}$, as **2**. The NMR data of **3** were identical to those of **2**, except for the upfield shifts of C-17 and C-23, both by −1.3 ppm, and the downfield shifts of C-20, C-21, and C-27 by +1.8, +2.2, and +1.3 ppm, respectively. This suggested that **3** was a geometric isomer of **2** at the C-20(22) double

bond. The configuration of the C-20(22) double bond in **3** was further confirmed to be of the *Z* form due to the NOESY correlation between the methyl proton at δ_H 2.08 (H-21) and the olefinic proton at δ_H 5.80 (H-22), as seen in the ROESY spectrum. Thus, compound **3** was determined to be 3β,12β,24,25-tetrahydroxy-23-methoxydammar-20(22)(*Z*)-ene-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside and named notoginsenoside ST-3.

Compound **4** had a molecular formula $C_{47}H_{80}O_{18}$ on the basis of the quasimolecular ion peak in the negative HRESIMS. Comparisons of the ^{1}H and ^{13}C NMR data with those of notoginsenoside Ft_1 (*25*) indicated that the only difference between them was the side chain. Both compounds presented the same degrees of unsaturation as eight; however, **4** had one more oxygen atom. Besides two quaternary oxygen-bearing carbon signals at δ_C 73.4 (C-20) and 69.9 (C-25), there were two olefinic methines [δ_C 123.9 (C-23) and 142.0 (C-24); δ_H 6.31 (H-23) and 6.02 (H-24)] in the side chain of **4**. The structure of the side chain was further established by an HMBC experiment, in which the long-range cross peaks from H-21 (δ_H 1.43) to C-17 (δ_C 54.2) and C-20 (δ_C 73.4); from H-22 (δ_H 2.78 and 2.49) to C-20, C-21 (δ_C 27.7), C-23, and C-24; from H-23 to C-22 (δ_C 40.1) and C-25 (69.9); and from H-24 to C-22, C-25, C-26 (δ_C 30.8), and C-27 (δ_C 30.8) were observed. It indicated that the double bond was located between C-23 and C-24, and two hydroxyl groups were at C-20 and C-25, respectively. The fragment ion peaks at *m/z* 932 $[M]^-$ and 800 $[M - 132]^-$ in the FABMS, along with the HMBC correlations of δ_H 4.93 (d, J = 7.5 Hz, H-1′) with δ_C 89.0 (C-3); δ_H 5.53 (d, J = 7.5 Hz, H-1″) with δ_C 83.0 (C-2′); and δ_H 5.39 (d, J = 6.5 Hz, H-1‴) with δ_C 84.6 (C-2″), confirmed the sugar moiety of **4** to be the same as that of notoginsenoside Ft_1. Hence, compound **4** was determined to be 3β,12β,20(*S*),25-tetrahydroxydammar-23-ene-3-*O*-β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside and named notoginsenoside ST-5.

On the basis of traditional Chinese medical theories, the herbs need processing after harvest for different purposes. The chemical compositions of the steamed notoginseng were significantly different from those in the raw materials. Because the process of steaming notoginseng was carried out under high temperature, the new monodesmosides should be formed by the degradation of the C-20 glycosyl moiety of the dammarane skeleton during the processing. It is apparent that the rich dammarane-type monodesmosides presented are not only chemically characteristic of steamed notoginseng but also give special biological activities to this processed herb. The pharmaceutical evaluation of the steamed notoginseng is now in progress.

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