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Letter

Saponins from Roots of *Panax notoginseng*

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ABSTRACT

Objective To study the chemical constituents in the dried roots of *Panax notoginseng*. **Methods** The constituents were isolated and purified with chromatographic methods. Their structures were elucidated by spectroscopic methods (1D, 2D NMR, UV, IR, $[\alpha]_D$, and HRESI-TOF-MS) and chemical analyses. **Results** Twenty saponins including 20(*S*)-ginsenoside Rh_1 (**1**), 6-*O*-β-*D*-(6′-acetyl)-glucopyranosyl-24-ene-dammar-3β, 6α,12β,20*S*-tetraol (**2**), ginseno- side Rf (**3**), notoginsenoside R_2 (**4**), ginsenoside Rg_2 (**5**), ginsenoside Rg_1 (**6**), notoginsenoside Rt (**7**), koryoginsenoside R_1 (**8**), 6-*O*-(β-*D*-glucopyranosyl)-20-*O*-(β-*D*-xylopyranosyl)-3β,6α,12β,20(*S*)-tetrahydroxy-dammar-24-ene (**9**), pseudoginsenoside Rt_3 (**10**), notoginsenoside R_1 (**11**), ginsenoside Re (**12**), notoginsenoside N (**13**), ginsenoside F_1 (**14**), ginsenoside U (**15**), ginsenoside Rk_3 (**16**), 3β,12β-dihydroxydammar-(*E*)-20(22),24-diene-6-*O*-β-*D*-xylopyranosyl-(1→2)-β-*D*-glucopyranoside (**17**), ginsenoside Rh_4 (**18**), pseudoginsenoside Rt_5 (**19**), and vinaginsenoside R_{22} (**20**) were obtained. **Conclusion** Compounds **2**, **19**, and **20** are isolated from this species for the first time. The ^{1}H-NMR data of compound **19** and ^{1}H-NMR and ^{13}C-NMR data of compound **20** are first reported. Meanwhile, the NMR data of β-*D*-xylopyranosyl group in compound **9** is corrected.

Key words

Araliaceae; *Panax notoginseng*; pseudoginsenoside Rt_5; saponins; vinaginsenoside R_{22}

1. Introduction

Panax notoginseng (Burk.) F. H. Chen (Araliaceae) is a Chinese medicinal herb, distributed throughout the southwest of China, Burma, and Nepal. It was first used by national minorities in southwest China and widely accepted during the Ming Dynasty. It has been reported to have antihypertensive, antithrombotic, anti-atherosclerotic, and neuroprotective activities (Ng, 2006; He et al, 2011). The dried roots of *P. notoginseng* are used for promoting blood circulation. There are various chemical constituents in the dried roots of *P. notoginseng*, including ginsenosides, notoginsenosides, flavonoids, volatile oils, amino acids, and polysaccharide (Gao and Zhe, 2010; Cao et al, 2013). In our studies on the constituents from this plant by using chromatographies such as silica gel, ODS, and HPLC, 20 known saponins were identified by the chemical and physical methods, especially spectral analyse. Among them, compounds **2**, **19**, and **20** were isolated from this species for the first time, and the NMR data of compound **20** were first reported. In this paper, the NMR data of all the compounds were determined by 1D and 2D NMR spectra including ^{1}H-^{1}H COSY, HSQC, HMBC, and HSQC-TOCSY, which would make up the lack of accuracy of data assignment elucidated

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only by ^{1}H-NMR and ^{13}C-NMR experiments. On the other hand, the data of the chemical constituents in the roots of *P. notoginseng* were supplemented, which could provide the basic data for the development and utilization of *P. notoginseng*.

2. Materials and methods

2.1 General

Optical rotations were measured on a Rudolph Autopol® IV Automatic Polarimeter (l = 50 mm), IR data were recorded on a Varian 640-IR FT-IR Spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were determined on a Bruker 500 MHz NMR Spectrometer (Avance III 500MR) at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR with tetramethylsilane (TMS) as internal standard. Positive-ion HRESI-TOF-MS was recorded on an Agilent Technologies 6520 Accurate-Mass Q-Tof LC/MS Spectrometer.

A highly-porous synthetic resin (D101) was purchased from Haiguang Chemical Co., Ltd. (Tianjin, China). Silica gel column chromatography (CC) was obtained from Qingdao Haiyang Chemical Co., Ltd., (48−75 μm, Qingdao, China). HPLC was performed on ODS (Cosmosil 5C18−MS−II, Tokyo, Japan; Φ = 20 mm, L = 250 mm, flow rate: 9.0 mL/min), and the eluate was monitored with a UV Detector (Shimadzu RID−10A UV-Vis, Japan). Pre-coated TLC plates with silica gel GF_{254} (Tianjin Silida Technology Co., Ltd., China) were used to detect the purity of the isolate achieved by spraying with 10% aqueous H_2SO_4-EtOH, followed by heating.

2.2 Plant materials

The dried roots of *Panax notoginseng* (Burk), F. H. Chen were collected from Wenshan, Yunnan province, China and identified by Dr. Tian-xiang Li. The voucher specimen (No. 20120505) was deposited at Tianjin University of Traditional Chinese Medicine.

2.3 Extraction and isolation

The dried roots of *P. notoginseng* (5.0 kg) were refluxed with 70% ethanol-water twice. Evaporation of the solvent under reduced pressure provided a 70% ethanol-water extract (480.2 g). The residue was dissolved in H_2O and subjected to D101 CC [EtOH-H_2O (0:100→50:50→100:0) to afford EtOH eluent. The EtOH eluent (120.0 g) was subjected to silica gel CC [$CHCl_3$→$CHCl_3$-MeOH (100:3→100:7)→$CHCl_3$-MeOH-H_2O (10:3:1→7:3:1→6:4:1, lower layer)] to give 12 fractions (Frs. 1—12). Fr. 7 (8.0 g) was subjected to silica gel CC and PHPLC to yield 20(*S*)-ginsenoside Rh_1 (**1**, 54.9 mg), 6-*O*-β-*D*-(6′-acetyl)-glucopyranosyl-24-en-dammar-3β,6α,12β,20*S*-tetraol (**2**, 36.9 mg), ginsenosides F_1 (**14**, 75.5 mg), Rk_3 (**16**, 50.2 mg), Rh_4 (**18**, 438.6 mg), and pseudoginsenoside Rt_5 (**19**, 4.4 mg). Fr. 8 (4.0 g) was separated by ODS CC and PHPLC CC, repeatedly. And notoginsenoside R_2 (**4**, 225.3 mg), notoginsenoside Rt (**7**, 40.3 mg), koryoginsenoside R_1 (**8**, 4.4 mg), 6-*O*-(β-*D*-glucopyranosyl)-20-*O*-(β-*D*-xylopyranosyl)-3β,6α,12β,20(*S*)-tetrahydroxydammar-24-ene (**9**, 20.0 mg), pseudoginsenoside Rt_3 (**10**, 7.6 mg), and 3β,12β-dihydroxy-dammar-(*E*)-20(22),24-diene-6-*O*-β-*D*-xylopyranosyl-(1→2)-β-*D*-glucopyranoside (**17,** 38.9 mg) were produced. Fr. 9 (16.0 g) was subjected to ODS CC and further purified by PHPLC to give notoginsenoside R_2 (**4**, 452.6 mg), ginsenoside Rg_2 (**5**, 426.1 mg). ginsenoside Rg_1 (**6**, 12.56 g), and 6-*O*-(β-*D*-glucopyranosyl)-20-*O*-(β-*D*-xylopyranosyl)-3β,6α,12β,20(*S*)-tetrahydroxydammar-24-ene (**9**, 19.0 mg). Fr. 10 (3.6 g) was subjected to ODS CC, silica gel CC, and PHPLC to give ginsenosides Rf (**3,** 10.7 mg), Rg_1 (**6**, 22.0 mg), Re (**12**, 108.1 mg), U (**15**, 30.7 mg), notoginsenosides R_1 (**11**, 992.2 mg) and N (**13**, 23.8 mg), 3β,6α-20(*S*)-6,20-bis(β-*D*-glucopyranosyloxy)-3-hydroxy dammar-24-en-12-one (**10**, 9.3 mg), and vinaginsenoside R_{22} (**20**, 23.9 mg).

3. Results and discussion

Compound **2**: white powder. Positive-ion HRESI-TOF-MS *m/z* 703.4409 $[M + Na]^+$ (calcd for $C_{38}H_{64}O_{10}Na$ 703.4392). ^{1}H-NMR (C_5D_5N, 500 MHz) δ: 0.95 (3H, s, H_3-30), 1.06 (3H, s, H_3-19), 1.25 (3H, s, H_3-18), 1.42 (3H, s, H_3-21), 1.55 (3H, s, H_3-29), 1.64 (3H, s, H_3-27), 1.66 (3H, s, H_3-26), 2.07 (3H, s, H_3-28), 3.51 (1H, dd, J = 4.5, 11.5 Hz, H-3), 3.93 (1H, m, H-12), 4.40 (1H, ddd, J = 3.0, 10.5, 10.5 Hz, H-6), 5.03 (1H, d, J = 8.0 Hz, H-1′), 5.32 (1H, t, J = 7.0 Hz, H-24). Compound **2** was identified as 6-*O*-β-*D*-(6′-acetyl)-glucopyranosyl-24-ene-dammar-3β,6α,12β,20*S*-tetraol by comparison of the physical, ^{1}H-NMR and ^{13}C-NMR data (Table 1) with the reported data (Jia and Wang, 2009).

Compound **9**: white powder. Positive-ion HRESI-TOF-MS *m/z* 793.4734 $[M + Na]^+$ (calcd for $C_{41}H_{70}O_{13}Na$ 793.4709). ^{1}H-NMR (C_5D_5N, 500 MHz) δ: 0.81 (3H, s, H_3-30), 1.03 (3H, s, H_3-19), 1.17 (3H, s, H_3-18), 1.52 (3H, s, H_3-26), 1.60 (3H, s, H_3-21), 1.63 (3H, s, H_3-29), 1.64 (3H, s, H_3-27), 2.06 (3H, s, H_3-28), 3.51 (1H, dd, J = 5.0, 11.5 Hz, H-3), 4.12 (1H, m, H-12), 4.42 (1H, ddd, J = 2.5, 10.5, 10.5, H-6), 5.01 (1H, d, J = 8.0 Hz, H-1′), 5.03 (1H, d, J = 8.0 Hz, H-1″), 5.29 (1H, t, J = 7.0 Hz, H-24). Compound **9** was identified as 6-*O*-(β-*D*-glucopyranosyl)-20-*O*-(β-*D*-xylopyranosyl)-3β,6α,12β,20(*S*)-tetrahydroxydammar-24-ene (Liu et al, 2011), but the ^{13}C-NMR data (Table 1) of β-*D*-xylopyranosyl in the compound should be corrected.

Compound **19**: white powder. Positive-ion HRESI-TOF-MS *m/z* 677.4238 $[M + Na]^+$ (calcd for $C_{36}H_{62}O_{10}Na$ 677.4235). ^{1}H-NMR (C_5D_5N, 500 MHz) δ: 0.77 (3H, s, H_3-30), 1.02 (3H, s, H_3-19), 1.20 (3H, s, H_3-18), 1.25 (6H, s, H_3-26 and 27), 1.46 (3H, s, H_3-21), 1.60 (3H, s, H_3-29), 2.07 (3H, s, H_3-28), 3.52 (1H, dd, J = 4.0, 11.5 Hz, H-3), 3.70 (1H, ddd, J = 5.0, 10.5, 10.5 Hz, H-12), 4.45 (1H, ddd, J = 3.0, 10.5, 10.5 Hz, H-6), 5.03 (1H, d, J = 8.0 Hz, H-1′), 4.10 (1H, t, J = 7.5 Hz, H-24); ^{1}H-NMR (CD_3OD, 500 MHz) δ: 0.98 (3H, s, H_3-30), 0.96 (3H, s, H_3-19), 0.99 (3H, s, H_3-29), 1.10 (3H, s, H_3-18), 1.27 (3H s, H_3-21), 1.22 (3H, s, H_3-26), 1.13 (3H, s, H_3-27), 1.32 (3H, s, H_3-28), 3.11 (1H, dd, J = 5.0, 12.0

Table 1 ^{13}C-NMR (125 MHz) data of compounds 1—11

Position	1	2	3	4	5	6	7	8	9	10	11
1	39.4	39.4	39.4	39.4	39.4	39.3	39.5	39.5	39.5	39.5	39.4
2	27.9	27.9	28.7	27.7	27.7	27.7	27.9	27.9	28.0	27.9	27.7
3	78.6	78.6	78.7	78.7	78.4	78.6	78.7	78.7	78.7	78.7	78.9
4	40.4	40.3	40.2	40.2	40.0	40.4	40.3	40.3	40.4	40.3	40.2
5	61.5	61.4	61.4	61.3	60.8	61.3	61.4	61.5	61.4	61.4	61.3
6	80.1	79.7	79.9	79.4	74.4	80.0	79.8	80.1	80.1	79.7	79.5
7	45.2	45.5	45.1	45.0	46.0	45.0	45.5	45.6	45.1	45.2	44.9
8	41.1	41.2	41.2	41.1	41.1	41.0	41.3	41.3	41.1	41.2	41.1
9	50.2	50.2	50.1	50.1	49.8	49.9	50.0	50.0	50.0	50.0	49.9
10	39.7	39.7	39.7	39.6	39.6	39.5	39.7	39.8	39.7	39.7	39.6
11	32.1	32.1	32.1	32.0	32.0	30.7	30.9	31.0	31.0	31.0	30.9
12	71.0	71.0	71.0	71.0	71.0	70.3	70.3	70.2	70.2	70.2	70.3
13	48.3	48.4	48.3	48.2	48.2	48.9	49.2	49.2	49.2	49.3	49.1
14	51.7	51.7	51.7	51.6	51.7	51.3	51.4	51.4	51.4	51.4	51.4
15	31.4	31.6	31.2	31.2	31.3	30.6	30.9	31.0	30.7	30.8	30.7
16	26.8	26.8	26.8	26.8	26.8	26.5	26.6	26.7	26.6	26.6	26.6
17	54.8	54.8	54.8	54.7	54.7	51.7	51.6	51.7	51.7	51.5	51.6
18	17.4	17.4	17.4	17.3	17.2	17.4	17.6	17.7	17.6	17.6	17.5
19	17.7	17.7	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.5
20	73.0	73.0	73.0	73.0	73.0	83.3	83.3	83.3	83.0	83.3	83.3
21	27.1	26.8	27.0	27.0	27.0	22.4	22.4	22.4	22.2	22.3	22.4
22	35.8	35.9	35.8	35.8	35.8	35.9	36.1	36.1	36.0	36.2	36.0
23	23.0	23.0	23.0	23.0	23.0	23.2	23.3	23.2	23.2	23.2	23.3
24	126.4	126.3	126.3	126.3	126.3	125.8	126.0	126.0	125.9	126.0	125.9
25	130.8	130.8	130.8	130.8	130.8	131.0	131.0	131.0	131.1	131.0	131.0
26	25.8	25.8	25.8	25.8	25.8	25.8	25.8	25.8	25.8	25.8	25.8
27	17.7	17.7	17.7	17.7	17.7	17.8	17.8	17.8	17.8	17.8	17.8
28	31.7	31.4	32.1	31.7	32.2	31.6	31.6	31.6	31.8	31.6	31.7
29	16.4	16.5	16.8	16.8	17.6	16.3	16.5	16.5	16.4	16.5	16.7
30	16.8	17.0	16.8	16.7	16.9	17.0	17.4	17.3	17.2	17.4	17.1
1′	106.1	105.9	103.9	103.5	101.8	105.8	105.9	106.1	106.0	106.7	103.5
2′	75.5	75.4	79.6	79.8	78.6	75.3	75.4	75.4	75.5	75.3	79.8
3′	79.6	79.2	79.9	80.1	79.4	79.4	79.2	79.2	79.7	79.4	80.0
4′	71.9	71.4	72.3	71.7	72.6	71.7	71.5	71.5	71.9	71.2	71.7
5′	78.1	75.1	77.9	78.0	78.4	77.9	75.1	75.2	78.1	67.1	78.0
6′	63.1	65.2	63.4	62.8	63.1	62.9	65.2	65.1	63.1		62.8
1″		170.9	103.8	104.7	101.9	98.1	98.3	98.3	98.9	98.3	104.7
2″		21.0	76.0	75.8	72.4	75.0	75.2	75.2	75.0	75.2	75.8
3″			78.4	78.8	72.3	78.9	79.3	79.3	79.2	79.2	78.7
4″			71.7	71.2	74.3	71.4	71.6	71.7	71.0	71.7	71.2
5″			78.1	67.2	69.5	78.1	78.3	78.3	67.1	78.3	67.2
6″			62.9		18.7	62.6	62.9	62.9		63.0	
1‴											98.2
2‴											75.1
3‴											79.2
4‴											71.5
5‴											78.2
6‴											62.9
CH_3CO							170.9				
CH_3CO							21.0				

Hz, H-3), 3.48 (1H, ddd, *J* = 5.0, 11.0, 11.0 Hz, H-12), 3.89 (1H, t, *J* = 7.5 Hz, H-24), 4.10 (1H, ddd, *J* = 3.0, 10.5, 10.5 Hz, H-6), 4.34 (1H, d, *J* = 8.0 Hz, H-1′). Compound **19** was identified as pseudoginsenoside Rt_5 by comparison of the physical, and ^{13}C-NMR data (Table 2) with the reported data (Tanaka et al, 1985), and the ^{1}H-NMR data reported here were determined by 1D and 2D NMR spectra.

Compound **20**: white powder. Positive-ion HRESI-TOF-MS (*m/z* 857.4850 $[M + Na]^+$, calcd for $C_{42}H_{74}O_{16}Na$ 857.4869). The ^{1}H-NMR (C_5D_5N, 500 MHz) spectrum of

Table 2 ^{13}C-NMR (125 MHz) data of compounds 12—20

Position	12	13	14[a]	14	15	16	17	18	19[a]	19	20
1	39.4	39.4	40.1	39.4	39.4	39.5	39.7	39.5	40.3	39.6	39.5
2	27.8	28.0	27.7	28.1	28.1	27.9	27.8	27.9	27.7	28.0	28.0
3	78.4	78.6	79.5	78.5	78.5	78.6	78.8	78.6	79.9	78.6	78.9
4	40.0	40.4	40.5	40.3	40.3	40.4	40.2	40.4	40.6	40.4	40.4
5	60.8	61.4	62.1	61.7	61.7	61.5	61.5	61.4	62.0	61.6	61.4
6	74.6	80.3	68.8	67.7	67.7	80.0	79.4	80.0	80.9	80.1	80.2
7	46.0	44.9	47.2	47.4	47.4	45.3	45.1	45.3	45.3	45.1	45.1
8	41.2	41.1	42.0	41.2	41.2	41.3	41.3	41.3	41.9	41.0	41.1
9	49.6	50.0	50.1	49.9	49.9	50.7	50.5	50.6	51.4	50.6	49.9
10	39.7	39.7	40.1	39.3	39.4	39.5	39.7	39.7	40.4	39.6	39.7
11	31.0	31.0	30.9	30.8	30.8	32.7	32.2	32.3	32.9	32.4	31.2
12	70.2	70.2	71.6	70.2	70.2	72.4	72.5	72.6	72.4	71.2	70.4
13	49.1	49.2	49.3	49.1	49.1	52.1	50.7	50.7	49.9	48.4	48.9
14	51.4	51.5	52.3	51.3	51.3	51.1	50.9	50.8	53.2	52.2	51.5
15	30.8	30.6	31.6	30.8	30.7	32.5	32.6	32.6	33.6	31.7	30.9
16	26.7	26.6	27.2	26.6	26.6	30.7	28.8	28.8	29.7	25.5	26.8
17	51.7	51.4	53.1	51.6	51.6	48.3	50.4	50.4	49.1	49.5	52.7
18	17.3	17.6	17.7	17.6	17.6	17.4	17.3	17.4	17.4	17.9	17.4
19	17.5	17.6	17.7	17.4	17.4	17.8	17.7	17.7	18.5	17.1	17.6
20	83.3	83.3	84.8	83.2	83.4	155.4	140.1	140.1	87.9	86.7	83.4
21	22.3	22.3	22.8	22.4	22.3	108.2	13.1	13.1	27.1	27.0	22.7
22	36.0	36.2	36.7	36.1	36.2	33.7	123.5	123.5	32.2	32.8	33.8
23	23.2	23.2	24.2	23.2	23.2	27.1	27.4	27.4	26.1	28.8	27.1
24	126.0	126.0	125.8	125.9	126.0	125.3	123.8	123.8	86.0	85.6	79.8
25	130.9	130.9	132.2	130.9	131.1	131.2	131.2	131.2	71.9	70.3	72.8
26	25.8	25.8	25.9	25.8	25.8	25.8	25.7	25.7	26.7	27.5	26.7
27	17.8	17.8	18.0	17.8	18.0	17.8	17.7	17.7	26.8	27.7	26.0
28	32.2	31.8	31.5	32.0	32.0	31.7	31.7	31.7	31.3	31.7	31.8
29	17.6	16.3	16.1	16.5	16.5	16.3	16.7	16.4	16.1	16.3	16.4
30	17.3	17.2	17.3	17.4	17.4	16.8	16.8	16.8	18.1	18.0	17.0
1′	101.9	105.7	98.2	98.2	98.0	106.0	103.5	106.0	105.6	106.0	106.0
2′	78.6	74.9	75.3	75.1	74.8	75.4	80.2	75.4	75.5	75.5	75.5
3′	79.4	78.9	78.2	79.2	79.2	79.6	79.8	79.6	79.1	79.7	79.7
4′	72.6	81.3	71.1	71.6	71.5	71.8	71.7	71.8	71.8	71.9	71.9
5′	78.3	76.5	77.9	78.2	77.0	78.1	78.0	78.0	77.7	78.2	78.1
6′	63.1	62.2	62.5	62.8	70.2	63.1	62.9	63.1	63.0	63.2	63.4
1″	101.9	103.1			105.3		104.8				98.3
2″	72.4	74.5			75.2		75.8				75.5
3″	72.3	75.5			78.3		78.7				78.6
4″	74.2	72.0			71.7		71.2				78.7
5″	69.5	75.3			78.3		67.2				63.1
6″	18.7	62.8			62.8						
1‴	98.3	98.2									
2‴	75.2	75.1									
3‴	79.2	79.4									
4‴	71.6	71.7									
5‴	78.2	78.3									
6‴	62.9	62.9									

[a]determined in CD_3OD, the others were determined in C_5D_5N

compound **20** showed the signals assignable to eight methyls [δ 0.73, 1.02, 1.10, 1.55, 1.56, 1.57, 1.60, 2.06 (3H each, all s, H_3-30, 19, 18, 27, 26, 21, 29, 28), four methines bearing oxygen function [δ 3.51 (1H, dd, J = 5.0, 11.0 Hz, H-3), 3.74 (1H, dd, J = 3.0, 8.0 Hz, H-24), 3.92 (1H, m, H-12), 4.40 (1H, ddd, J = 3.0, 10.5, 10.5 Hz, H-6)], together with two anomeric proton signals shown at δ 5.00 (1H, d, J = 8.0 Hz, H-1′), 5.22 (1H, d, J = 7.5 Hz, H-1″). The ^{13}C-NMR spectrum displayed 42 carbons including 30 carbons for the aglycon, 12 carbons for two β-*D*-glucopyranosyl moieties. ^{1}H-NMR and ^{13}C-NMR spectra suggested that compound **20** was a dammarane-type triterpene saponin derivative. The chemical shift of δ 61.4 (C-5) indicated that compound **20** was a protopanaxatriol type saponin [δ 56 and 61 (C-5) for protopanaxadiol and protopanaxatriol type saponin, respectively]. The ^{1}H-^{1}H COSY experiment on compound **20** indicated the presence of partial structure written in bold lines. And in HMBC experiment, long-range correlations were observed between the following protons and carbons: H_3-18 and C-7–9, 14; H_3-19 and C-1, 5, 9, 10; H_3-21 and C-17, 20, 22; H_3-26 and C-24, 25, 27; H_3-27 and C-24–26; H_3-28 and C-3–5, 29; H_3-29 and C-3–5, 28; H_3-30 and C-8, 13–15; H-1′ and C-6; H-1″ and C-20. The stereochemistry of C-20 in compound **20** was clarified to be *S* by comparing the chemical shifts of 20–22-carbons of it with those of compounds **12**–**15**. The absolute configuration of C-24 (δ 79.8) was identified as 24*R* on comparison with the chemical shift values of cyclounifolioside C (24*R*, C-24: δ 80.3) and cyclocantogenin (24*S*, C-24: δ 77.0) (Zhao et al, 2008). On the basis of the above mentioned evidence, compound **20** was elucidated to be vinaginsenoside R_{22} (Duc et al, 1999), which was reported to presence in vietnamese ginseng by Duc et al, but there was no NMR data were given. In this paper, the NMR data were reported for the first time. The ^{1}H-NMR (C_5D_5N, 500 MHz) δ: 0.73 (3H, s, H_3-30), 1.02 (3H, s, H_3-19), 1.10 (3H, s, H_3-18), 1.55 (3H, s, H_3-27), 1.56 (3H, s, H_3-26), 1.57 (3H, s, H_3-21), 1.60 (3H, s, H_3-29), 2.06 (3H, s, H_3-28), 3.51 (1H, dd, J = 5.0, 11.0 Hz, H-3), 3.74 (1H, dd, J = 3.0, 8.0 Hz, H-24), 3.92 (1H, m, H-12), 4.40 (1H, ddd, J = 3.0, 10.5, 10.5 Hz, H-6), 5.00 (1H, d, J = 8.0 Hz, H-1′), 5.22 (1H, d, J = 7.5 Hz, H-1″).

The structures of 20(*S*)-ginsenoside Rh_1 (**1**) (Li et al, 2010), ginsenoside Rf (**3**) (Sun et al, 2009), notoginsenoside R_2 (**4**) (Dou et al, 2003), ginsenoside Rg_2 (**5**) (Sun et al, 2009), ginsenoside Rg_1 (**6**) (Teng et al, 2002), notoginsenoside Rt (**7**) (Li et al, 2007), koryoginsenoside R_1 (**8**) (Kim et al, 1995), pseudoginsenoside Rt_3 (**10**) (Liu et al, 2011), notoginsenoside R_1 (**11**) (Zeng et al, 2007), ginsenoside Re (**12**) (Zeng et al, 2007), notoginsenoside N (**13**) (Yoshikawa et al, 2001), ginsenoside F_1 (**14**) (Guo, Fi, and Dou, 2006), ginsenoside U (**15**) (Sun et al, 2005), ginsenoside Rk_3 (**16**) (Park et al, 2002), 3β,12β-dihydroxydammar-(*E*)-20(22),24-diene-6-*O*-β-*D*-xylopyranosyl-(1→2)-β-*D*-glucopyranoside (**17**) (Chen et al, 2007), and ginsenoside Rh_4 (**18**) (Zeng et al, 2007) were identified by comparison of the physical, ^{1}H-NMR, and ^{13}C-NMR data (Tables 1 and 2) with the reported data, respectively.

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