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A novel hexanordammarane glycoside from the leaves and stems of Panax quinquefolium L.

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A novel hexanordammarane glycoside from the leaves and stems of *Panax quinquefolium* L.

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One novel hexanordammarane glycoside, ginsenoside R_{10}, was isolated from the leaves and stems of *Panax quinquefolium* L. as a minor constituent. It is the first time that a hexanordammarane glycoside isolated from the plant of *Panax quinquefolium* L. Its structure was elucidated as 3-*O*-*β*-D-glucopyranosyl-3*β*, 12*β*-dihydroxy-22, 23, 24, 25, 26, 27-hexanordammarane-20-one (**1**), by the combination analysis of one-dimensional NMR, two-dimensional NMR and mass spectrometry.

Keywords: *Panax quinquefolium* L.; hexanordammarane; ginsenoside R_{10}

1. Introduction

It was reported that the leaves and stems of *Panax quinquefolium* L. showed similar medical effects as the roots of *Panax quinquefolium* L. such as anti-hemorrhagic shock, protective effect against liver injury and anticancer (Mo, 2001; G. Y. Li, Zeng, Meng, X. Li, & Wang, 2009). The chemical compositions of the leaves and stems of *P. quinquefolium* were also investigated in the recent research such as quinquenoside L_3 (Wang, W. Li, & X. Li, 1998), quinquenoside L_9 (Wang et al., 2001), quinquenosides L_{10}, L_{14} and L_{16} (Chen et al., 2009). As part of an ongoing research on the chemical constituents of the leaves and stems of *Panax quinquefolium* L., this article describes the isolation and the structural elucidation of a new hexanordammarane minor constituent, ginsenoside R_{10} (**1**), by the chemical and spectroscopic methods (1D and 2D NMR, MS). The structure of **1** has been determined as 3-*O*-*β*-D-glucopyranosyl-3*β*, 12*β*-dihydroxy-22, 23, 24, 25, 26, 27-hexanordammarane-20-one. It is the first time that a hexanordammarane glycoside is isolated from the plant of *Panax quinquefolium* L.

2. Results and discussion

Repeated CC of the *n*-BuOH extract partition of the water extract of the leaves and stems of *Panax quinquefolium* L. led to the isolation of a new hexanordammarane glycoside (**1**).

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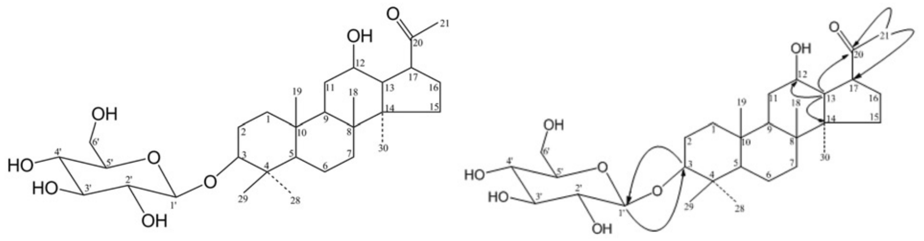

Figure 1. The structure and HMBC correlations of glycoside **1**.

Compound **1** was obtained as white amorphous solid (MeOH) that gave positive reaction to the Libermann–Burchard test. HR-ESI-MS: m/z 537.3447 $[M-H]^-$ (calcd for 537.3506), indicated the molecular formula of **1** to be $C_{30}H_{50}O_8$. Acid hydrolysis of 1 with 1.0 M aqueous HCl yielded D-glucose as the only sugar component. The ^1H NMR spectra of **1** displayed six methyl singlet signals at δ 0.76 (3H, s), δ 0.92 (3H, s), δ 0.95 (3H, s), δ 0.98 (3H, s), δ 1.31 (3H, s), δ 2.40 (3H, s). The sugar was determined as β-glucose by the proton (δ 4.94, d, $J = 7.5$ Hz) in the ^1H NMR spectrum and an anomeric carbon signal at δ 107.1, respectively. Except for the signals of a glucopyranosyl unit, the aglycone of compound **1** revealed the presence of five *tert*-methyls, seven methylenes, six methines (two of them were oxygen substituted), four quaternary carbons as well as one methyl ketone. In comparison with a normal dammarane saponin ginsenoside Rh_2 (Figure 1), isolated from the roots of *Panax quinquefolium* L. and *ginseng* whose aglycone was protopanaxadiol, the chemical shifts of **1** showed close resemblance with those of ginsenoside Rh_2 (Kitagawa, Yoshikawa, & Yoshihara, 1983), except the signals caused by the side-chain. In the case of glycoside **1**, the presence of a methyl ketone (δ 213.5 and δ 30.7) was observed, instead of the carbon signals of the side-chain (C-20, 21, 22, 23, 24, 25, 26 and 27). The side-chain's chemical shifts of **1** showed close resemblance with those of notoginsenoside R_{10} (Li, Teng, & Yang, 2001) and $3\beta,6\alpha,12\beta$-triol-22, 23, 24, 25, 26, 27-hexanordammaran-20-one (Wu et al., 2007). The ^{13}C NMR data of **1** compared with ginsenoside Rh_2 and notoginsenoside R_{10} suggested the presence of a methyl ketone as notoginsenoside R_{10}.

In the HMBC spectrum, the long-range correlation between the methyl proton signal at δ 2.40 (H-21) and the carbon signals at δ 213.5 (C-20) and δ 52.9 (C-17) could be identified. Moreover, the HMBC spectrum also showed the long-range correlation between the proton signal at δ 2.37 (H-13) and the carbon signals at δ 71.4 (C-12), δ 51.6 (C-14) and δ 213.5 (C-20). In addition, the long-range correlation between the proton signal at δ 0.92 (3 H, s, H-30) and the carbons at δ 33.0 (C-15), 40.3 (C-8), δ 0.95 (3 H, s, H-18) and δ 40.3 (C-8), 35.6 (C-7), 51.6 (C-14) could also be identified in the HMBC correlations. So, the aglycone of **1** was considered to have a hexanor- dammarane skeleton with carbonyl oxygen linked on C-20. The location of the *O*-β-D-glucopyranosyl unit was determined to be on C-3 of the aglycone by 2DNMR spectra (Figure 2), and by analysis of two-dimensional NMR spectra, the proton and carbon signals of **1** were assigned based on the above evidence. The structure of **1** could be characterised as 3-*O*-(β-D-glucopyranosyl)-3β, 12β-dihydroxy-22, 23, 24, 25, 26, 27-hexanordammarane-20-one. Compound **1** is a

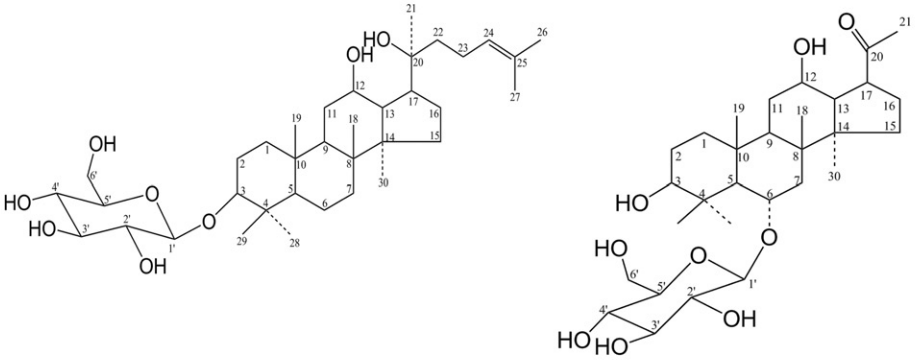

Figure 2. The structures of ginsenoside Rh_2 and notoginsenoside R_{10}.

minor glycoside in the leaves and stems of *Panax quinquefolium* L. It is the first time that a hexanordammarane glycoside is isolated from the plant of *Panax quinquefolium* L. From the viewpoint of biogenetic pathway, this special nortriterpenoid derivative may correspond to a pregnane skeleton (Li et al., 2001).

3. Experimental

3.1. *General experimental procedures*

HR-ESI-MS spectrum was recorded by using Ionspec 7.0 TFT-ICR-MS (IonSpec Corporation, Lake Forest, CA, USA). NMR spectra were measured at 500 MHz for ^{1}H NMR, 125.8 MHz for ^{13}C NMR, and 500 MHz for HMBC and HMQC on a Bruker Avance-500 spectrometer (Karlsruhe, Germany). NMR spectra were measured in pyridine-d_5 by using TMS as the internal standard (Cambridge Isotope Laboratories, Inc., Andover, MA, USA). Chemical shifts (δ) are expressed in ppm. Preparative HPLC was carried out on a 2998 Photodiode Array Detector and SunFire Prep C18 Column (10 µm, 10 × 150 mm), 1525 BINARY HPLC PUMP (Waters), the mobile phase was MeOH–H_2O (73 : 27), flow rate: 1.0 mL min^{-1}, detection wavelength: 203 nm. Silica gel H (200–300 mesh; Qingdao Marine Chemical, Inc., Qingdao, China) was used in column chromatography. Also, silica gel G plates (Qingdao Marine Chemical, Inc.) were used in thin layer chromatography.

3.2. *Plant material*

The leaves and stems of *P. quinquefolium* L. were collected in the Jingyu County of Jilin Province (China) in September 2007, and identified by Prof Jin-Min Zhang. A voucher specimen (No. 20070908) has been deposited at the Institute of Frontier Medical Science, Jilin University, China.

3.3. *Extraction and isolation*

Air-dried leaves and stems of *P. quinquefolium* L. (2.5 kg) were extracted with hot water (25 L × 3) and the water soluble fraction was extracted with $CHCl_3$ and *n*-BuOH in turn. The n-BuOH extract part was subjected to macro-reticular absorption resin (D101), and was eluted with H_2O (50 L) and 95% EtOH (50 L), and then afforded the EtOH fraction (388 g). A part of the EtOH fraction (150 g) was subjected to Si-gel CC eluting with $CHCl_3$–MeOH mixture to give 120 fractions. Fractions No. 78–83 was then subjected to preparative HPLC MeOH–H_2O (65 : 35) to obtain compound **1** (11 mg, 0.007%).

3.4. *NMR data of compound 1*

Compound 1: ^{1}H NMR (500 MHz, pry-d_5): δ 1.49 (1H, m, H-1e), δ 0.79 (1H, m, H-1a), δ 2.23 (1H, m, H-2e), δ 1.82 (1H, m, H-2a), δ 3.37 (1H, dd, $J = 11.5$, 4.5 Hz, H-3), δ 0.72 (1H, m, H-5), δ 1.51 (1H, m, H-6e), δ 1.35 (1H, m, H-6a), δ 1.45 (1H, m, H-7e), δ 1.19 (1H, m, H-7a),δ 1.40 (1H, m, H-9), δ 1.37 (1H, m, H-11e), δ 1.24 (1H, m, H-11a), δ 3.83 (1H, m, H-12), δ 2.37 (1H, d, $J = 9.0$ Hz, H-13), δ 1.96(1H, m, H-15e), δ 1.40 (1H, m, H-15a), δ 1.97 (1H, m, H-16e), δ 1.78 (1H, m, H-16a), δ 3.08 (1H, m, H-17), δ 0.95 (3H, s, H-18), δ 0.76 (3H, s, H-19), δ 2.40 (3H, s, H-21), δ 1.31 (3H, s, H-28), δ 0.98 (3H, s, H-29), δ 0.92 (3H, s, H-30), δ 4.94 (1H, d, $J = 7.5$ Hz, H-1′), δ 4.04 (1H, m, H-2′), δ 4.24 (1H, m, H-3′), δ 4.22 (1H, m, H-4′), δ 4.02 (1H, m, H-5′), δ 4.59 (1H, m, H-6′), δ 4.41 (1H, m, H-6′).

^{13}C NMR (125.8 MHz, pyr-d_5): δ 39.3 (C-1), δ 26.8 (C-2), δ 88.8 (C-3), δ 39.8 (C-4), δ 56.5 (C-5), δ 18.5 (C-6), δ 35.6 (C-7), δ 40.3 (C-8), δ 51.1 (C-9), δ 37.2 (C-10), δ 30.1 (C-11), δ 71.4 (C-12), δ 55.0 (C-13), δ 51.6 (C-14), δ 33.0 (C-15), δ 27.7 (C-16), δ 52.9 (C-17), δ 15.8 (C-18), δ 16.6 (C-19), δ 213.5 (C-20), δ 30.7 (C-21), δ 28.2 (C-28), δ 16.8 (C-29), δ 17.1 (C-30), δ 107.1 (C-1′), δ 75.9 (C-2′), δ 78.9 (C-3′), δ 72.0 (C-4′), δ 78.5 (C-5′), δ 63.2(C-6′).

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