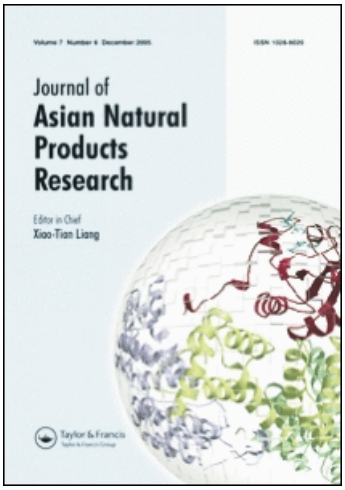


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# A New Saponin from the Leaves and Stems of *Panax quinquefolium* L. Collected in Canada

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*Note*

# A NEW SAPONIN FROM THE LEAVES AND STEMS OF *PANAX QUINQUEFOLIUM* L. COLLECTED IN CANADA

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A new dammarane-type saponin named quinquenoside L3 (**1**) together with vina-ginsenoside R3 (**2**) were isolated from the leaves and stems of *Panax quinquefolium* L. collected in Canada. On the basis of physicochemical and spectral evidences, **1** was established as 3-O-$\beta$-D-glucopyranosyl-20-O-[$\beta$-D-xylopyranosyl-(1 → 6)-$\beta$-D-glucopyranosyl] 20(S)-dammar-23-ene-3$\beta$, 12$\beta$,20,25-tetryol.

*Keywords:* *Panax quinquefolium* L.; Dammarane saponin; Quinquenoside L3 (**1**); Vina-ginsenoside R3 (**2**)

## INTRODUCTION

During the course of our studies on the saponin composition of the leaves and stems of *Panax quinquefolium* L., we recently reported the isolation and characterization of eleven known compounds and two new saponins, named quinquenoside L1 and L2 [1–3]. The present paper deals with the isolation and structural elucidation of a new dammarane-type saponin, quinquenoside L3 (**1**).

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## RESULTS AND DISCUSSION

Chromatography on silica gel and preparative HPLC on ODS of the n-BuOH-soluble portion of the boiling water extract of dried leaves and stems of *P. quinquefolium* led to the isolation of a new saponin quinquenoside L3 (**1**) together with a known compound vina-ginsenoside R3 (**2**) which was first isolated from *Panax vietamensis* Ha et Grushv in 1994 [4].

Quinquenoside L3 (**1**), $C_{47}H_{80}O_{18}$, mp 201–205°C, was obtained in 0.004% yield. Acid hydrolysis of **1** with 10% $H_2SO_4$ gave glucose and xylose as the sugar constituents. The $^{13}C$ NMR spectral data (Table I) supported a dammarane-type triterpenoid for **1**. The $^1H$ NMR spectrum of **1** showed the presence of eight tertiary methyl groups ($\delta$ 1.60, 1.54(6H), 1.31, 1.00(6H), 0.91, 0.83) and an axial methine proton at C-3 ($\delta$ 3.43, dd, $J = 10.6$ Hz); a double bond at C-23 was deduced from the two olefinic proton signals ($\delta$ 6.17, m, H-23; $\delta$ 6.07, d, $J = 15.6$ Hz, H-24), two vinylic proton signals ($\delta$ 3.10, $\delta$ 2.89, H-22), as well as the olefinic carbon resonances ($\delta$ 122.92, C-23; $\delta$ 142.39, C-24). The $^{13}C$ NMR spectrum of the aglucone

TABLE I $^{13}C$ NMR data for quinquenoside L3 (**1**) and vina-ginsenoside R3 (**2**) (75.4 MHz in pyridine-d5)

| *No.* | (1) | (2) | *No.* | (1) | (2) |
|---|---|---|---|---|---|
| 1 | 39.29 | 39.27 | 27 | 30.73 | 17.83 |
| 2 | 26.85 | 26.76 | 28 | 28.28 | 28.03 |
| 3 | 89.01 | 88.96 | 29 | 17.35 | 15.71 |
| 4 | 39.78 | 39.69 | 30 | 16.90 | 16.74 |
| 5 | 56.55 | 56.36 | | 20-glc | 3-glc |
| 6 | 18.58 | 18.41 | 1′ | 98.28 | 105.05 |
| 7 | 35.22 | 35.62 | 2′ | 75.17 | 83.47 |
| 8 | 40.20 | 40.27 | 3′ | 78.82 | 78.00 |
| 9 | 49.65 | 50.98 | 4′ | 71.71 | 71.66 |
| 10 | 37.08 | 36.93 | 5′ | 76.90 | 77.91 |
| 11 | 30.99 | 21.87 | 6′ | 70.10 | 62.85 |
| 12 | 70.62 | 25.51 | | 20-xyl(P) | 3-glc |
| 13 | 50.27 | 42.52 | 1″ | 105.59 | 106.02 |
| 14 | 51.59 | 50.62 | 2″ | 74.89 | 77.06 |
| 15 | 30.66 | 31.50 | 3″ | 77.98 | 78.16 |
| 16 | 26.50 | 28.03 | 4″ | 71.18 | 71.99 |
| 17 | 52.12 | 48.47 | 5″ | 67.04 | 77.19 |
| 18 | 16.39 | 16.56 | 6″ | | 63.13 |
| 19 | 16.16 | 16.44 | | 3-glc | 20-glc |
| 20 | 83.46 | 82.22 | 1‴ | 106.98 | 98.59 |
| 21 | 23.33 | 21.57 | 2‴ | 75.86 | 75.61 |
| 22 | 39.69 | 40.63 | 3‴ | 78.93 | 79.01 |
| 23 | 122.92 | 23.18 | 4‴ | 72.00 | 71.60 |
| 24 | 142.39 | 126.09 | 5‴ | 78.39 | 78.31 |
| 25 | 70.10 | 130.61 | 6‴ | 63.19 | 62.70 |
| 26 | 30.73 | 25.76 | | | |

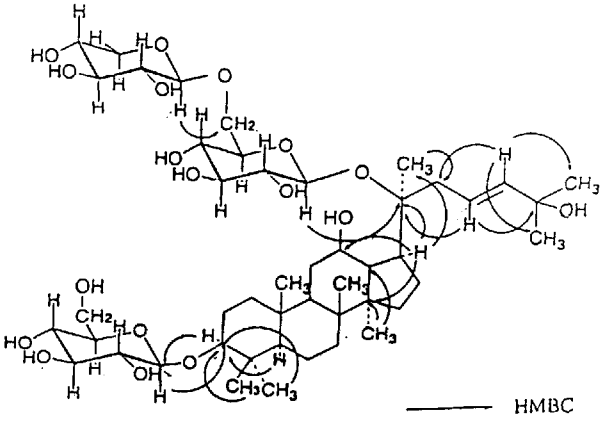


FIGURE 1 HMBC correlations for quinquenoside L3 (**1**).



moiety of (**1**) was in coincidence with that of aglucone moiety of vinaginsenoside $R_8$ [4]. The sugar sequence and the interglycosidilic linkage was determined by HMBC (Fig. 1).

The $^1$H NMR spectrum of **1** displayed three anomeric proton signals at $\delta$ 5.15 (d, $J=7.5$ Hz, 20-glc-1′H), $\delta$ 5.50 (d, $J=7.0$ Hz, 6′-xyl-1″H), $\delta$ 4.95 (d, $J=7.5$ Hz, 3-glc-1‴H). In the HMBC spectrum, the anomeric proton signals at $\delta$ 5.15 (20-glc-1′H), $\delta$ 5.50 (xyl-1″H), $\delta$ 4.95 (3-glc-1‴H) were in correlation with the carbon signals of C-20 ($\delta$ 82.96), 20-glc-6′C ($\delta$ 70.12), C-3 ($\delta$ 88.48), respectively, while the proton signals of H-3 ($\delta$ 3.34), 20-glc-6′H ($\delta$ 4.72) correlated with the anomeric carbon signals at $\delta$ 106.64 (3-glc-1‴C) and $\delta$ 105.26 (6′-xyl-1″C) (Fig. 2). According to the coupling constants of the anomeric protons, and the chemical shifts of the carbon signals, all sugars have typical $\beta$-linkage. All of above evidences led to the formulation of **1** as 3-O-$\beta$-D-glucopyranosyl-20-O-[$\beta$-D-xylopyranosyl-(1 → 6)-$\beta$-D-glucopyranosyl] 20(S)-dammar-23-ene-3$\beta$,12$\beta$,20,25-tetryol.

## EXPERIMENTAL

*General experimental procedures* Melting points were measured on a Yamco micro-hot-state and uncorrected. All NMR spectra were recorded on Bruker-ARX 300 spectrometers, using TMS as an internal standard. For HPLC, a Shimadazu CTO-6A apparatus with ODS-5 (20 mm i.d. × 25 cm) column and UV-detector were used. Chromatographic and silica gel

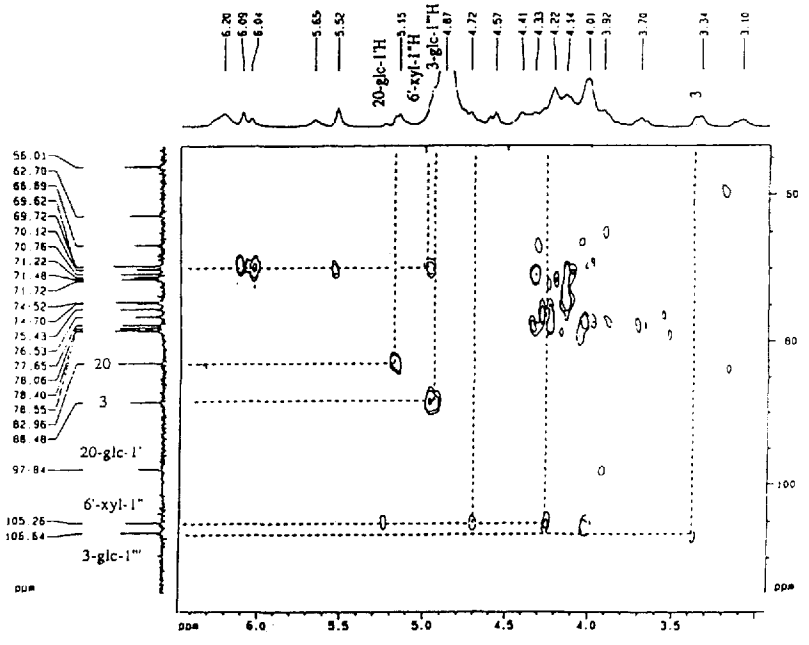


FIGURE 2 HMBC specturm of quinquenoside L3.

are all produced by Qingdao Ocean Chemical Factory; Diaion D101 was produced by Tianjin Second Reagent Factory.

*Plant material* The leaves and stems of *P. quinquefolium* L. were collected in Canada. The plant material was identified by Prof. Qin Tiande, Liaoning Provincial Institute for Drug Controls, and deposited in the Dalian Tianma Pharmaceutical Factory.

*Extraction and isolation* Dried and finely powdered leaves and stems of the plant (2.0 kg) were extracted with boiling water. After filtration, the extract was evaporated to 20 L, and fractionated with $CHCl_3$, EtOAc and t-BuOH successively. The t-BuOH extract was subjected to column chromatography on D101, using $H_2O$, 70% MeOH, and MeOH as solvents to give a $H_2O$ fraction, a 70% MeOH fraction (312 g), and a MeOH fraction. Part of the 70% MeOH fraction (100 g) was chromatographed on silica gel using $CHCl_3$–MeOH (7 : 1) as eluent to yield fraction A and $CHCl_3$–MeOH (5 : 1) to yield fraction B. Fraction B was subjected to HPLC on ODS column (20 mm i.d. × 25 cm) using 70% MeOH as mobile phase to give compound **1** (0.004% yield) and from the elution using 75% MeOH as mobile phase, compound **2** was obtained.

*Quinquenoside L3* (**1**) White needles from MeOH, mp 201–205°C, $^1$H NMR (300 MHz, in $C_5D_5N$): $\delta$ 6.17 (m, 23H); 6.07 (d, $J = 15.6$ Hz, 24H); 3.43 (dd, $J = 10.6$ Hz, 3H); 3.10, 2.89 (22H); 1.60 (3H, s, 21-$CH_3$); 1.54 (6H, s, 26- and 27-$CH_3$); 1.31 (3H, s, 28-$CH_3$); 1.00 (6H, s, 18- and 29-$CH_3$); 0.91 (3H, s, 30-$CH_3$); 0.83 (3H, s, 19-$CH_3$); 5.15 (d, $J = 7.5$ Hz, 20-glc-1′H), 5.50 (d, $J = 7$ Hz, 6′-xyl-1″H), 4.95 (d, $J = 7.5$ Hz, 3-glc-1‴H), and $^{13}$C NMR (75.4 MHz, in $C_5D_5N$): see Table I.

*Vina-ginsenoside R3* (**2**) White needles from MeOH, mp 252–254°C, $^1$H NMR (300 MHz, in $C_5D_5N$): $\delta$ 5.31 (1H, br, t, $J = 7$ Hz, 24H); 3.33 (dd, $J = 10.4$ Hz, 3H); 1.67 (3H, s, 21-$CH_3$); 1.66 (3H, s, 26- and 27-$CH_3$); 1.51 (3H, s, 28-$CH_3$); 1.28 (3H, s, 18- and 29-$CH_3$); 1.11 (3H, s, 30-$CH_3$); 0.97 (6H, s, 19-$CH_3$); 0.78 (3H, s); 5.10 (d, $J = 7.5$ Hz, 20-glc-1‴H), 5.37 (d, $J = 7.0$ Hz, 3-xyl-1′H), 4.93 (d, $J = 7.5$ Hz, 3-glc-1″H), 1.67; 1.66; 1.51; 1.28; 1.11; 0.78 (each 3H); 0.97 (6H). $^{13}$C NMR (75.4 MHz, in $C_5D_5N$): see Table I.

*Acid hydrolysis of* **1** Compound **1** (2.5 mg) was hydrolyzed with 10% $H_2SO_4$ in MeOH–$H_2O$ (1 : 1) at 80°C for 4 h. The reaction mixture was neutralized with $Ba(HCO_3)_2$, filtrated and the filtrate evaporated to dryness *in vacuo* to give a residue in which glucose and xylose were identified by TLC [5].



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We are grateful to the Dalian Tianma Pharmaceutical Factory for collecting plants from Canada. Thanks are also due to Prof. Qin Tiande for identification of the plant.

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