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QUINQUENOSIDE L₉ FROM LEAVES AND STEMS OF *PANAX QUINQUEFOLIUM* L.

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During additional chemical investigation on the saponin composition of leaves and stems of *Panax quinquefolium* L., a new minor dammarane saponin, quinquenoside L₉ (1) has been obtained. By means of physico-chemical evidences and spectral analysis, its structure was elucidated as 6-O-[α -L-rhamnopyranosyl-(1-2)- β -D-glucopyranosyl]-dammara-3 β ,6 β ,12 β ,20(S),24 ζ ,25-hexaol (1).

Keywords: *Panax quinquefolium* L.; Leaves and stems; *Araliaceae*; Chemical study; Triterpenoid saponin; Quinquenoside L₉

INTRODUCTION

American ginseng (the root of *Panax quinquefolium* L.) is well known for its tonic value worldwide, the leaves and stems of *Panax quinquefolium* L. also show similar medical effects in recent research. Chemical investigations on them have been reported by us [1, 2]. In a continuation of investigation on saponin composition of leaves and stems of *Panax quinquefolium* L., we report here the isolation and structural elucidation of another new minor saponin, quinquenoside L₉.

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RESULTS AND DISCUSSION

Quinquenoside **L**₉ (**1**) was isolated by silica gel column chromatography and HPLC of the saponin fractions in a yield of 0.00003%.

Quinquenoside L₉ (**1**) was obtained as white needles, mp 155~157°C (MeOH). Liebermann-Burchard and Molish reactions were positive. The quasimolecular ion peaks at *m/z* 819.5125 (C₄₂H₇₄O₁₅H, calcd. 819.5106), 841.4949 (C₄₂H₇₄O₁₅Na, calcd. 841.4925) in the HR-LRMS of **1** allowed its molecular formula to be C₄₂H₇₄O₁₅.

Saponin (**1**) showed a close resemblance with ginsenoside Rg₂ [3] in their ¹³CNMR spectra (100 MHz, C₅D₅N), the only difference between them was observed in the side-chains. Ginsenoside Rg₂, which has a common side-chain in ginsenosides, showed resonances at δ126.28 and δ130.78 for C-24 and C-25, respectively, while saponin **1** had no double-bond carbon signal. The ¹H NMR spectral data (400 MHz, C₅D₅N) of saponin **1**, indicated that saponin **1** has a 24,25-dihydroxyl moiety as vina-ginsenoside -R₁₂ and -R₁₃ [4]. The coupling system of this side-chain was established as follows. In the ¹H-¹H COSY spectrum of **1**, two geminal proton signals at δ2.07 and δ2.21 (H-23) correlated not only with the proton signal at δ3.82 (1H, *dd*, *J*=7.0, 4.0 Hz, H-24), but also with other two geminal proton signals at δ1.75 and δ2.49 (H-22). In the HMBC spectrum of **1**, long-range correlations were observed between the proton signal at δ3.82 (H-24) and two methyl carbon signals at δ25.85, 26.09 (C-26, 27), δ33.62 (C-22) and δ72.69 (C-25), and between the methyl proton signal at δ1.42 (H-21) and carbon signals at δ54.42 (C-17) and δ33.62 (C-22). Up to these points it could be concluded that the two hydroxyl groups might be located at C-24 and C-25. By comprehensive analyses of 2D-NMR spectra, the ¹H and ¹³CNMR spectral data of **1** were unequivocally assigned as shown in Table I.

Acid hydrolysis of saponin **1** yielded D-glucose and L-rhamnose. The ¹H and ¹³CNMR spectra demonstrated that saponin **1** has a β-D-glucopyranosyl and an α-L-rhamnopyranosyl moieties. In the HMBC spectra, the long-range correlations were observed between an anomeric proton signal at δ5.26 (*d*, *J*=7.2 Hz, glc-1') and carbon signal at δ74.33 (C-6), and between an other anomeric proton signal at δ6.48 (*br.s*, rham-1'') and the carbon signal at δ78.52 (glc-2'). Thus, the structure of saponin **1** was established as 6-O-[α-L-rhamnopyranosyl-(1-2)-β-D-glucopyranosyl]-dammara-3β,6α,12β,20(S),24ζ,25-hexaol, named quinquenoside **L**₉.

TABLE I The NMR data of quinqueoside L₉ (I)

No.	¹ H	¹³ C	COSY	HMBC	No.	¹ H	¹³ C	COSY	HMBC
1	0.59, 1.63	39.36	H-2		23	2.07, 2.21	26.67	H-22, 24	
2	1.7 ~ 1.9	27.70	H-1, 3		24	3.82(<i>dd</i> , 7.0, 4.0 Hz)	80.07	H-23	C-22, 25, 26, 27
3	3.48(<i>dd</i> , 6.0, 2.0 Hz)	78.28	H-2		25		72.69		
4		39.93		C-4, 28, 29	26	1.50 (3H, <i>s</i>)	25.85		C-24, 25, 27
5	1.49	60.76	H-6	C-4, 6, 19	27	1.53 (3H, <i>s</i>)	26.09		C-24, 25, 26
6	4.68(<i>br.t.</i> , 6.0 Hz)	74.33	H-5, 7		28	2.11 (3H, <i>s</i>)	32.13		C-3, 4, 5, 29
7	1.96, 2.25	45.98	H-6		29	1.35 (3H, <i>s</i>)	17.59		C-3, 4, 5, 29
8		41.12			30	0.94 (3H, <i>s</i>)	16.86		C-8, 13, 14, 15
9	1.53	49.77	H-11		6-glc				
10		39.57			1'	5.26(<i>d</i> , 7.2 Hz)	101.73	H-2'	
11	1.46, 2.08	32.01	H-12		2'	4.38	78.52	H-1', 3'	C-6
12	3.88(<i>dt</i> , 7.0, 2.5 Hz)	70.96	H-11, 13		3'	4.33	79.34	H-2', 4'	
13	2.03	48.07	H-12, 17		4'	4.21	72.51	H-3', 5'	
14		51.68			5'	3.96	78.28	H-4', 6'	
15	0.87, 1.50	31.40	H-16		6'	4.35	63.10	H5'	
16	1.27, 1.81	26.97	H-15, 17		2'-rham				
17	2.31	54.42	H-13, 16		1''	6.48(<i>br.s</i>)	101.87	H-2''	C-2'
18	1.17 (3H, <i>s</i>)	17.07		C-13, 20, 21	2'	4.79	72.36	H-1'', 3''	
19	0.96 (3H, <i>s</i>)	17.53		C-7, 8, 9, 14	3''	4.66	72.24	H-2'', 4''	
20		73.21		C-1, 5, 9, 10	4''	4.32	74.12	H-3'', 5''	
21	1.42 (3H, <i>s</i>)	27.34		C-17, 20, 22	5''	4.95	69.38	H-4'', 6''	
22	1.75, 2.49	33.62	H-23		6''	1.78(3H, <i>d</i> , 6.0 Hz)	18.65	H-5''	C-4'', 5''

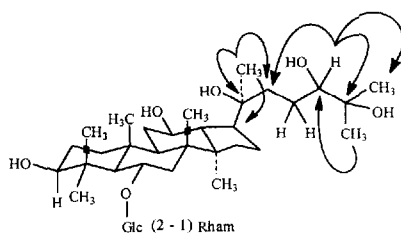


FIGURE 1 HMBC correlations of quinquenoside L₉ (1).

EXPERIMENTAL SECTION

General Experimental Procedures

The melting point was determined on Yanaco MP-S3 Micro-hot stage and are uncorrected. HR-MS data were taken on a JEOL JMS-700T spectrometer. UV spectrum was taken in MeOH on Shimadzu UV-260 spectrophotometers. NMR spectra were taken in pyridine-*d*₅ on a JEOL JNM-GX 400 spectrometer, 2D-NMR experiments were carried out with standard pulse sequences. For HPLC (Shimadzu-6A system), a Shimadzu CTO-6A apparatus with ODS (20 mm i.d., 25 cm) column and UV-detector was used. For CC, silica gel H (10–40 μ, Qingdao) and highly porous polymer D101 (Qingdao) were used. Hydrolysis of saponin with mineral acid and identification of the resulting sugar with TLC were performed as described by Zhao [5].

Plant Material

The leaves and stems of *Panax quinquefolium* L. were collected from Canada by Dalian Tianma Pharmacy Co. LTD, and identified by Professor Tiande Qing.

Extraction and Separation of Saponins

Dried leaves and stems of *Panax quinquefolium* L. (2.0 Kg) were extracted with hot water (201 × 3), the water soluble fraction was extracted successively with CHCl₃ and *n*-BuOH. The *n*-BuOH soluble fraction was subjected to column chromatography on reversed-phase highly porous polymer, D101 (2.0 Kg), with H₂O (40 l) and 95% EtOH (40 l) as eluting

solvents, affording a H₂O fraction and an EtOH fraction (312 g). A part of the EtOH fraction (100 g) was chromatography over silica gel {gradient elution with CHCl₃-MeOH [100:1 (I); 100:2 (II); 100:8 (III); 100:9 (IV); 100:12 (V); 100:15 (VI, VII); 100:18 (VIII); 100:20 (IX); 100:30 (X); 100:40 (XI)]} to provide eleven fractions in increasing order of polarity. Fraction VIII was separated into ten fractions, frs. VIII *a* – VIII *j*, by HPLC (ODS, solvent: 75% MeOH, flow rats: 4 ml min⁻¹; detection UV at 198 nm.). From frs. VIII *h*, saponin **1** was obtained as white needles (0.00003% yield).

Quinquenoside L₉ (1), white needles, mp 155~157°C (MeOH). Liebermann-Burchard and Molish Reactions were positive. LR-MS: 819 (M+H), 841 (M+Na), HR-MS: 819.5125 (C₄₂H₇₅O₁₅H, cal. 819.5106), 841.4949 (C₄₂H₇₂O₁₅Na, cal. 841.4925), ¹H-NMR (400 MHz, C₅D₅N) and ¹³C-NMR (100 MHz, C₅D₅N) data see Table I.

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We are grateful to Professor Tiande Qing for identification of the plant material. Thanks also for Dalian Tianma Pharmacy Co. LTD.

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