

## A Novel Hexanordammarane Glycoside from the Roots of *Panax notoginseng*

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**Abstract:** Notoginsenoside R<sub>10</sub>, a novel hexanordammarane glycoside was isolated from the roots of *Panax notoginseng*, as a minor constituent. Its structure was determined as 6-O-( $\beta$ -D-glucopyranosyl)-3 $\beta$ ,6 $\alpha$ ,12 $\beta$ -trihydroxy-22,23,24,25,26,27-hexanordammaran-20-one(**1**), by means of spectroscopic methods.

**Keywords:** Notoginsenoside R<sub>10</sub>, nortriterpenoid saponin, *Panax notoginseng*.

There are extensive chemical studies on the roots of *Panax notoginseng* (Burk.) F. H. Chen, a famous traditional Chinese medicine called San-Qi or Tian-Qi, thirty-three dammarane saponins were isolated and their structures were identified by our group and other scientists<sup>1-8</sup>. Further chemical investigation on this plant led to the isolation of a novel hexanordammarane glycoside, named notoginsenoside R<sub>10</sub> (**1**).

Notoginsenoside R<sub>10</sub> (**1**), white powder, negative HRFAB-MS showed a quasimolecular ion at  $m/z$  553.331[M-H]<sup>-</sup>. Negative FAB-MS gave a fragment ion at  $m/z$  391 [M-162-H]<sup>-</sup> which suggested the presence of a hexosyl unit in the sugar moiety. Together with the NMR data the molecular formula was indicated as C<sub>30</sub>H<sub>50</sub>O<sub>9</sub> (calcd. 553.337). <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** exhibited an anomeric proton signal at  $\delta$  4.99 (1H, d, J=7.76) and an anomeric carbon signal at  $\delta$  105.9 respectively. Except the signals of a glucopyranosyl unit, the aglycone of compound **1** revealed the presence of five *tert*-methyls, six methylenes, seven methines (three of them were oxygen substituted), four quaternary carbons, as well as one methyl ketone. In comparison with a normal dammarane saponin ginsenoside Rh<sub>1</sub> (**2**), isolated from the roots of *P. notoginseng* and *P. Ginseng* whose aglycone is protopanaxatriol, the chemical shifts of **1** showed close resemblance with those of **2**, except the signals caused by the side-chain. In the case of glycoside **1**, the presence of a methyl ketone ( $\delta$  213.4 and  $\delta$  30.4) was observed, instead of the carbon signals of the side-chain (C-20, 21, 22, 23, 24, 25, 26 and 27).

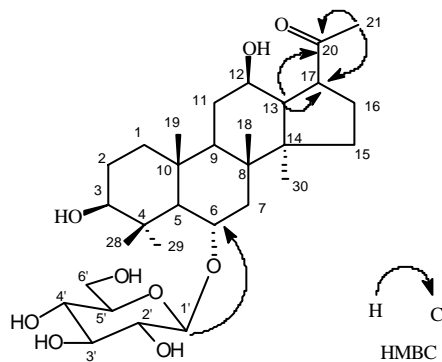
HMQC and HMBC experiments showed correlation between H-21 with C-20 and

C-17; H-13 with C-17 and C-20. So, the aglycone of **1** was considered to have a hexanordammarane skeleton with a carbonyl oxygen linked on C-20. The location of the O- $\beta$ -D-glucopyranosyl unit was determined to be on C-6 of the aglycone by 2D NMR spectra (**Figure 1**). All  $^{13}\text{C}$  chemical shifts of **1** were assigned by comparison with those of **2** (**Table 1**), and by analysis of two-dimensional NMR spectra, the proton signals of **1** were unequivocally assigned as shown in **Table 2**. Based on the above evidence, the structure of **1** could be characterized as 6-O-( $\beta$ -D-glucopyranosyl)-3 $\beta$ ,6 $\alpha$ ,12 $\beta$ -trihydroxy -22,23,24,25,26,27-hexanordammarane-20-one. Compound **1** is a minor glycoside in the roots of *P. notoginseng* whose content is less than 0.1 ppm. It is the first time that a nordammarane glycoside is isolated from a plant of *Panax*, a very famous genus in herbal medicine. From the viewpoint of biogenetic pathway, this special nortriterpenoid derivative may correspond to a pregnane skeleton.

**Table 1**  $^{13}\text{C}$  NMR chemical shifts of compounds **1** and **2** in  $\text{C}_5\text{D}_5\text{N}$  ( $\delta$  in ppm)

C	1	2	C	1	2
1	39.6	39.5	19	17.8	17.7
2	28.0	28.0	20	213.5	73.1
3	78.6	78.7	21	30.41	27.1
4	40.4	40.4	22		35.9
5	61.5	61.5	23		23.1
6	80.0	80.1	24		126.4
7	45.6	45.3	25		130.8
8	41.3	41.2	26		25.9
9	50.9	50.3	27		17.7
10	39.8	39.8	28	31.8	31.8
11	32.9	32.2	29	16.4	16.4
12	71.4	71.1	30	16.9	16.9
13	52.9	48.4	Glc 1'	106.0	106.0
14	51.4	51.7	2'	75.5	75.6
15	31.0	31.3	3'	79.6	79.6
16	27.7	26.9	4'	72.0	72.1
17	54.4	54.8	5'	78.0	78.1
18	17.4	17.5	6'	63.2	63.3

**Figure 1** Long-range correlation of glycoside **1** from HMBC



**Table 2**  $^1\text{H}$  NMR chemical shifts of compound **1** in  $\text{C}_5\text{D}_5\text{N}$ ( $\delta$  in ppm,  $J$  in Hz)

H	1
Aglycone	
1	1.64 (1H, <i>m</i> )
	1.00 (1H, <i>m</i> )
2	1.86(1H, <i>m</i> )
	1.67(1H, <i>m</i> )
3	3.51(1H, <i>dd</i> , $J=11.4, 4.8$ )
5	1.43(1H, <i>br, s</i> )
6	4.45(1H, <i>ddd</i> , $J=10.0, 10.0, 2.6$ )
7	2.50(1H, <i>dd</i> , $J=12.7, 2.9$ )
	1.90(1H, <i>t</i> , $J=11.8$ )
9	1.56(1H, <i>m</i> )
11	2.06(1H, <i>m</i> )
	1.51(1H, <i>br, s</i> )
12	3.85(1H, <i>m</i> )
13	3.05(1H, <i>m</i> )
15	1.55(1H, <i>m</i> )
	1.20(1H, <i>m</i> )
16	1.78(1H, <i>m</i> )
	1.35(1H, <i>m</i> )
17	2.34(1H, <i>m</i> )
18	1.16(3H, <i>s</i> )
19	0.97(3H, <i>s</i> )
21	2.37(3H, <i>s</i> )
28	2.05(3H, <i>s</i> )
29	1.58(3H, <i>s</i> )
30	0.76(3H, <i>s</i> )
glyco	
1'	5.00(1H, <i>d</i> , $J=7.8$ )
2'	4.08(1H, <i>t</i> , $J=8.2$ )
3'	4.23(1H, <i>t</i> , $J=8.6$ )
4'	4.19(1H, <i>t</i> , $J=8.8$ )
5'	3.92(1H, <i>m</i> )
6'	4.50(1H, <i>dd</i> , $J=11.5, 2.3$ )
	4.34(1H, <i>dd</i> , $J=11.1, 5.4$ )

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