Chinese Chemical Letters Vol. 13, No. 3, pp 251 – 252, 2002 251
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Monepaloside K, a New Triterpenoid Saponin from *Morina nepalensis* var. *alba* Hand. - Mazz.

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Abstract: One new triterpenoid saponin, monepaloside K (**1**) was isolated from the water-soluble part of the whole plant of a famous Tibetan medicinal herb, *morina nepalensis* var. *alba* Hand.-Mazz.. Its structure was determined to be 3-O-α-L-arabinopyranosyl-(1→3)-β-D-xylopyranosyl siaresinolic acid on the basis of spectroscopic evidences, especially 2D NMR techniques.

Keywords: *Morina nepalensis* var. *alba*, *Dipsacaceae*, monepaloside K, 2D NMR techniques.

Morina nepalensis var. *alba* Hand.-Mazz., belonging to the family *Dipsacaceae* and genus *Morina*, is a famous Tibetan traditional medicinal herb in China and has been used for the treatment of many diseases since ancient time[1,2]. Although sterols, triterpenes, alkaloids, flavanoids, phenylpropanol derivatives and so on have been found in *Morina* plants[3-7], the chemical constituents of *M. nepalensis* var. *alba* Hand. - Mazz. and the water-soluble chemical constituents of *Morina* palnts have not been reported. From the water-soluble fraction of the whole plant of *M. nepalensis* var. *alba*, one new triterpenoid saponin, monepaloside K (**1**) was isolated and identified.

Monepaloside K (**1**), white powder, mp: 177 - 179°C; $[\alpha]_D^{26}$ +0.88 (*c* 0.29, MeOH). Its negative ion HR-FABMS showing a quasi-molecular peak at *m/z* 735.4281 $[M-H]^-$ established its molecular formula as $C_{40}H_{64}O_{12}$(calcd. for $C_{40}H_{63}O_{12}$: 735.4320) which was also confirmed by negative ion FABMS showing a molecular peak at *m/z* 736 $[M]^-$ and ^{13}C NMR (DEPT) spectrum. In the ^{13}C NMR spectrum (**Table 1**), the signals due to the aglycon moiety were in good agreement with those of the ilexoside A methyl ester (3-O-β-D-xylopyranosyl siaresinolic acid methyl ester) except C-28[8]. Chemical shift of C-28 (180.88 ppm) in **1** showed that C-28 was carboxyl group and not esterified. Consequently **1** was considered as a C-3 monodesmoside of siaresinolic acid. It is worth noting that the chemical shift of H-19 (δ 3.59, brs).

The ^1H NMR spectrum of **1** exhibited two anomeric proton signals at δ 4.77 (d, 7.2 Hz) and δ 5.25 (d, 7.2 Hz). In the meantime, ^{13}C NMR spectrum exhibited two anomeric carbon signals at δ 107.32 and δ 106.00. So **1** has one more sugar than ilexoside A[8]. In HMQC-TOCSY spectrum, ^{13}C signals of this sugar were at δ 106.00, 74.45, 72.79, 69.37, 67.38 respectively, and similar to those of α-L-arabinopyranosyl[9-12]. In ROESY spectrum of **1**, H-3 and H-5_b of this sugar were found to be correlated with its

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anomeric proton H-1, which confirmed the α-configuration of its anomeric proton. The 6.7 Hz (> 5 Hz) coupling constant of $^{3}J_{(H\text{-}1,\ H\text{-}2)}$ also confirmed the α-configuration[11,12].

Compared ^{13}C NMR data of **1** with ilexoside A methyl ester, C-3 of xylopyranosyl in **1** was shifted downfield from δ 78.58 to δ 86.87[8]. It suggested that the arabinopyranosyl was linked at C-3 of xylopyranosyl which also was confirmed by ROESY spectrum showing NOE correlation between ara H-1 (δ 5.25, d, 7.2 Hz) and xyl H-3 (δ 4.13). Furthermore, NOE correlation between xyl H-1 (δ 4.77, d, 7.2 Hz) and H-3 (δ 3.30, dd, 4.2 Hz, 11.6 Hz) of the aglycon was also detected in ROESY spectrum. So the structure of **1** was elucidated to be 3-O-α-L-arabinopyranosyl-(1→3)-β-D-xylop--yranosyl siaresinolic acid.

Figure 1 Key information from ROESY spectrum of monepaloside K

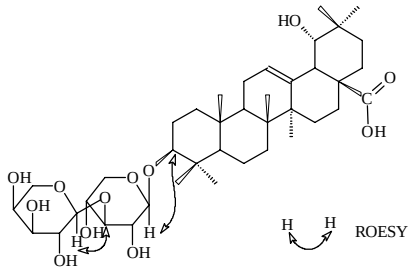

Table 1 ^{13}C NMR data of saponin **1** (125 MHz, pyridine-d_5)

C		C		C		C		C		C	
1	38.63	8	40.05	15	28.90	22	33.36	29	28.90	ara-1	106.00
2	26.72	9	48.34	16	28.41	23	28.11	30	24.11	2	72.79
3	88.95	10	37.23	17	46.12	24	16.91	xyl-1	107.32	3	74.45
4	39.65	11	24.20	18	44.84	25	15.47	2	74.50	4	69.37
5	55.00	12	123.16	19	81.16	26	17.52	3	86.87	5	67.38
6	18.69	13	144.87	20	35.77	27	24.88	4	69.37		
7	33.70	14	42.20	21	29.22	28	180.88	5	66.60		

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Received 17 August, 2001