Chinese Chemical Letters Vol. 15, No. 1, pp 46 – 48 , 2004
http://www.imm.ac.cn/journal/ccl.html

Three New Dammarane Glycosides from *Gynostemma pentaphyllum*

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Abstract: Three new dammarane-type glycosides (**1-3**) had been isolated from the aerial part of *Gynostemma pentaphyllum* (Thunb) Makino. The structures of compounds **1-3** had been elucidated as 3β, 12β, 25-trihydroxy-20(S), 24(S)-epoxydammarane 3-*O*-β-D-glucopyranosyl (1→2)-β-D-xylo -pyranoside, 3β, 12β, 25-trihydroxy-20(S), 24(R)-epoxydammarane 3-*O*-β-D-glucopyranosyl (1→2) -β-D-xylopyranoside and 3β, 12β, 23β, 25-tetrahydroxy-20(S), 24(S)-epoxydammarane 3-*O*-β-D- glucopyranosyl (1→2)-β-D-xylopyranoside, respectively, on the basis of chemical and spectro -scopic methods.

Keywords: *Gynostemma pentaphyllum*, dammarane-type glycoside.

Gynostemma pentaphyllum is a perennial creeping herb and widely distributed in China, Korea, Japan and Southeast Asia. The aerial part of this plant has been used as a folk medicine in China for the treatment of cough, asthma, chronic tracheitis, contagious hepatitis, and cancers[1]. In order to find out bioactive constituents we had isolated the ethanol extract of this plant and afforded three new compounds **1-3**, whose structures were determined by 1D and 2D NMR (HMQC, HMBC, H-H DQF COSY), FAB-MS and hydrolysis methods.

The ethanol extract of the plant was concentrated and filtered to give a solution. The solution was chromatographed on D 101 macroporous resin column to give a fraction containing the mixture of saponins. The fraction was submitted to silica gel and C_{18} columns, respectively, to give compounds **1-3**.

The FABMS of compound **1** showed a quasi-molecular ion $[M+H]^+$ at *m/z* 771, consistent with a molecular formula of $C_{41}H_{70}O_{13}$. The ^1H and ^{13}C NMR spectra (**Table 1**) suggested the presence of a triterpene moiety and two sugar residues, clearly indicated by two anomeric protons (δ 5.28 and 4.74) and two anomeric carbons (δ 106.1 and 105.9). Upon acid hydrolysis, compound **1** afforded 20(S)-protopanaxadiol oxide II, identified by comparison of the NMR data with literature values [2], and D-glucose and D-xylose. Glycosidation shift could be observed in C-3 position by comparing its ^{13}C NMR data with those of the aglycon [3]. The sequence and linkage position of the sugar chain could be characterized by HMBC experiment. Thus, in the HMBC spectrum, correlation peaks

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Figure 1 Chemical structures of compounds **1**-**3**

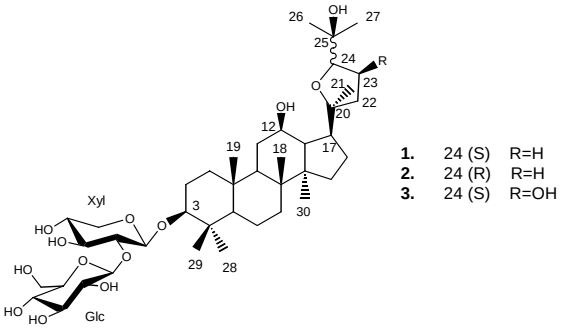

Table 1 ^{13}C NMR data of **1**-**3** (δ ppm)[a]

Carbon	**1**	**2**	**3**	Carbon	**1**	**2**	**3**
1	39.6	39.4	39.6	22	33.0	33.0	42.4
2	27.2	27.1	27.2	23	29.0	29.0	71.1
3	88.6	88.8	89.0	24	89.0	85.8	91.6
4	40.1	40.0	40.2	25	70.3	70.5	70.5
5	56.8	56.7	56.8	26	26.9	27.5	26.8
6	18.9	18.7	18.8	27	29.3	27.9	30.0
7	35.5	35.4	35.5	28	28.4	28.3	28.3
8	40.3	40.2	40.1	29	17.0	16.9	17.0
9	50.9	51.0	50.9	30	18.4	18.6	18.4
10	37.4	37.2	37.3				
11	33.0	31.9	32.8	Xyl 1	105.9	105.8	105.8
12	71.1	71.3	70.7	2	83.3	83.5	83.2
13	49.7	48.6	49.8	3	78.2	78.2	78.1
14	52.6	52.4	52.5	4	71.2	71.2	71.1
15	32.5	32.7	32.8	5	67.0	66.9	66.9
16	26.2	25.8	28.9	Glc 1	106.1	106.2	106.1
17	49.8	50.0	50.2	2	77.3	77.3	77.2
18	16.0	15.9	16.9	3	78.6	78.5	78.5
19	16.9	16.8	15.9	4	71.9	71.8	71.8
20	87.3	86.8	85.4	5	78.4	78.2	78.2
21	27.3	27.2	28.0	6	63.0	62.8	62.9

[a] Recorded in pyridine-d_5. Assignments were established by DEPT, HMQC and HMBC spectra.

between H-1 of xylose (δ 4.74) and C-3 of aglycone (δ 88.6), and H-1 of glucose (δ 5.28) and C-2 of xylose (δ 83.3) were observed. Consequently, compound **1** was a new triterpene glycoside whose structure was elucidated as 3β, 12β, 25-trihydroxy-20(S), 24(S)-epoxydammarane 3-*O*-β-D-glucopyranosyl (1→2)-β-D-xylopyranoside.

The FABMS of compound **2** displayed a quasi-molecular ion peak at *m/z* 771[M+H]$^+$, suggesting the same molecular formula as **1**. The ^{1}H and ^{13}C NMR spectra (**Table 1**) showed the presence of a triterpene moiety and two sugar residues, clearly indicated by two anomeric protons (δ 5.36 and 4.83) and two anomeric carbons (δ 106.2 and 105.8). The chemical shift values of its ^{13}C NMR signals attributable to aglycone were similar to those of **1** except signals belonging to C-24 (-3.2), C-27 (-1.4) and C-13 (-1.1), suggesting that the configuration at C-24 was *R* [2]. Glycosidation shift in C-3 position suggested the sugar chain was linked to C-3 of aglycone. In the HMBC spectrum,

correlation peaks between H-1 of xylose (δ 4.83) and C-3 of aglycone (δ 88.8), and between H-1 of glucose (δ 5.36) and C-2 of xylose (δ 83.5) were observed. Hence, the structure of **2** was identified as 3β, 12β, 25-trihydroxy-20(S), 24(R)-epoxydammarane 3-*O*-β-D-glucopyranosyl (1→2)-β-D-xylopyranoside.

The FABMS of compound **3** showed a quasi-molecular ion $[M+H]^+$ at *m/z* 787, consistent with a molecular formula of $C_{41}H_{70}O_{14}$. Acid hydrolysis of **3** afforded 3β, 12β, 23β, 25-tetrahydroxy-20(S), 24(S)-epoxydammarane, identified by comparison of the NMR data with literature values [4], and glucose and xylose. The ^{13}C and DEPT NMR spectra (**Table 1**) of **3** displayed 41 signals, of which 30 were assigned to a triterpene moiety and 11 to the saccharide portion. Analysis of the NMR data of **3** and comparison with those of **1** and **2** revealed that the compound had the same glycosidic chain at C-3 position of aglycone as in **1** and **2**. Further information was derived from the results of an HMBC experiment. In the HMBC spectrum, correlation peaks between H-1 of glucose (δ 5.33) and C-2 of xylose (δ 83.2), and between H-1 of xylose (δ 4.80) and C-3 of aglycone (δ 89.0) could be observed. On the basis of these evidences, the structure of **3** was elucidated as 3β, 12β, 23β, 25-tetrahydroxy-20(S), 24(S)-epoxydammarane 3-*O*-β-D-glucopyranosyl (1→2)-β-D-xylopyranoside.

Acknowledgment

The authors thank Prof. Liu Xiaolong of Wuhu School of Chinese Traditional Medicine for assistance in the collection and identification of the plant material and Dr. Laura Cao (HKUST) for providing FABMS data.

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Received 30 December, 2002