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Two new dammarane-type sapogenins from *Gynostemma pentaphyllum*

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Abstract

Two new sapogenins, named (20*S*, 24*R*)-3β,20,21β,25-tetrahydroxy-21,24-cyclodammarane (**1**) and 3β-hydroxyetio-17β-dammaranic acid (**2**), were isolated from the alkaline hydrolysate of *Gynostemma pentaphyllum* saponins. Their structures were elucidated by spectroscopic methods.

Keywords: *Gynostemma pentaphyllum*; Sapogenin; Alkaline hydrolysate

Gynostemma pentaphyllum (Thunb.) Makino, commonly called Jiaogulan in China, is an herbaceous vine of the family Cucurbitaceae widely cultivated in China, southern Korea and Japan. This plant has been reported to contain a number of dammarane-type glycosides, which were structurally closely similar to ginseng saponins [1–3]. Dammarane-type triterpenoids have been reported to show various biological activities, especially antitumor effect [4–6]. Previous studies of the structure–activity relationship between the ginsenosides and antitumor activity showed that the aglycones were more effective than the glycosides, and that the presence of sugar moieties reduced the antitumor activity [7]. In order to search for diversity of new bioactive metabolites from this plant species, in connection with our study, we mainly describe the structure elucidation of two new sapogenins from the alkaline hydrolysate of total saponins from *G. pentaphyllum* in this paper.

The total saponins of *G. pentaphyllum* (150 g) produced in Shanxi province were hydrolyzed for 12 h at 120 °C in a solution of ten times the amount of EtOH contained 30% NaOH, which was finished in an airtight and high pressure container without oxygen. The hydrolyzed products (45 g) were purified by silica gel column chromatography using an eluant of PE-acetone (20:1→1:1) as solvent and then repeated chromatographed over silica gel column and Sephadex LH-20 column to yield compound **1** (24 mg), compound **2** (53 mg).

Compound **1** was obtained as white amorphous powder. $[\alpha]_D^{20}$ +0.17 (*c* 0.27, CH_3OH). Its molecular formula was deduced as $C_{30}H_{52}O_4$ by the HR-TOF-MS (*m/z* 499.3759 $[M+Na]^+$, calcd. for $C_{30}H_{52}O_4Na$ 499.3758). The IR spectrum showed strong absorption at 3419 cm^{-1}, suggestive of the presence of hydroxyl group. In the ^1H NMR spectrum (300 MHz, in C_5D_5N, see Table 1) of compound **1**, seven methyl signals at δ_H 0.86 (s, 3H), 0.89 (s, 3H), 1.00

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Table 1
The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectral data of compound **1** and **2** (δ in ppm, J in Hz).

No.	Compound 1				Compound **2**		
	δ_C[a]	δ_C[b]	δ_H[a]	HMBC	δ_C[a]	δ_H[a]	HMBC
1	39.7	38.8	1.59 (m), 0.92 (m)	19	39.7	1.59 (m), 0.90 (m)	19
2	28.4	28.2	1.87 (m), 1.78 (m)	1	28.3	1.83 (m), 1.72 (m)	1
3	78.1	76.9	3.43 (dd, J = 10.3, 6.2)	4, 28, 29	78.1	3.43 (t, J = 7.5)	2, 4, 22
4	39.7	38.7			39.7		
5	56.5	55.6	0.8 (m)	4, 6, 28, 29,	56.4	0.79 (m)	3, 6, 21, 22
6	18.8	18.0	1.56 (m), 1.43 (m)	4, 5, 10	18.8	1.56 (m), 1.43 (m)	4, 5, 10
7	35.8	35.1	1.57 (m), 1.24 (m)	5, 6, 10	36.0	1.52 (m), 1.24 (m)	5, 6, 10
8	40.7	40.5			40.8		
9	51.3	50.4	1.35 (m)	5, 10, 19	51.2	1.33 (m)	5, 10, 19
10	37.5	36.8			37.5		
11	21.9	21.2	1.50 (m), 1.47 (m)	13	21.6	1.52 (m), 1.47 (m)	13
12	25.8	24.9	1.78 (m), 1.58 (m)	13, 15	26.1	2.03 (m), 1.38 (m)	13, 15
13	44.1	43.2	1.94 (m)	12, 15, 30, 20	46.9	2.26 (m)	17, 20
14	50.3	49.6			50.3		
15	31.9	30.6	1.58 (m), 1.09 (m)	12, 14, 17, 30	32.0	1.75 (m), 1.14 (m)	12, 14, 17, 23
16	27.8	27.3	2.03 (m), 1.88 (m)	13, 14, 15, 20	26.9	2.20 (m), 2.10 (m)	13, 14, 15, 20
17	47.6	46.0	2.13 (m)	20, 22	46.9	2.70 (m)	16, 13, 20
18	15.8	15.4	1.00 (s, 3H)	7, 8, 14	15.8	0.94 (s, 3H)	7, 8, 14
19	16.4	15.9	0.86 (s, 3H)	1, 5, 9, 10	16.6	0.82 (s, 3H)	1, 5, 9, 10
20	83.3	82.6			179.4		
21	77.9	76.4	4.23 (d, J = 9.1)	17, 24, 25	28.8	1.22 (s, 3H)	3, 4, 5, 22
22	32.1	31.1			16.4	1.02 (s, 3H)	3, 4, 5, 21
23	22.7	21.4			16.0	0.88 (s, 3H)	13, 14, 15
24	54.5	53.4	2.54 (m)	21, 23, 25, 26,27			
25	71.7	70.4					
26	29.8	28.5	1.54 (s, 3H)	24, 25, 27			
27	27.6	27.0	1.46 (s, 3H)	24, 25, 26			
28	28.7	28.2	1.22 (s, 3H)	3, 4, 5, 29			
29	16.5	16.2	1.04 (s. 3H)	3, 4, 5, 28			
30	16.5	16.1	0.89 (s, 3H)	8, 13, 14, 15			

[a] Measured in Pyr-d_6.
[b] Measured in DMSO-d_6.

(s, 3H), 1.04 (s, 3H), 1.22 (s, 3H), 1.46 (s, 3H), 1.54 (s, 3H) and two oxygenated methine proton signals at δ_H 3.43 (dd, 1H, J = 10.3, 6.2 Hz), 4.23 (d, 1H, J = 9.1 Hz) were exhibited. In addition, no signals from olefinic or sugar moiety were evident. From the ^{13}C NMR (75 MHz, in C_5D_5N) spectrum, 30 carbons were revealed, including four diagnostic oxygen-bearing carbon signals at δ_C 83.3, 78.1, 77.9, 71.9. Detailed comparison of the ^{1}H NMR and ^{13}C NMR spectra of **1** with (20*S*)-3β, 20, 21ξ, 25-tetrahydroxy-21, 24ξ-cyclodammarane 3-*O*-{[α-L-rhamnopyranosyl-(1→2)][β-D-xylopyranosyl(1→3)]-β-D-6-*O*-acetylglucopyranoside [8], a known dammarane saponin, indicated that compound **1** should be the aglycone of it. This result could be testified by the upfield shift of C-3 (-11) and also confirmed by HSQC and HMBC (Fig. 1) spectra, in which the following long-range correlations were observed: from H-3 (δ_H 3.43) to C-4 (δ_C 39.7), C-28 (δ_C 28.7), C-29 (δ_C 16.5), from H-17 (δ_H 2.13) to C-20 (δ_C 83.3), C-22 (δ_C 32.1), from H-21 (δ_H 4.23) to C-17 (δ_C 47.6), C-24 (δ_C 54.5), C-25 (δ_C 71.7), from H-24 (δ_H 2.54) to C-21 (δ_C 77.9), C-23 (δ_C 22.7), C-25 (δ_C 71.7), C-26 (δ_C 29.8), C-27 (δ_C 27.6). Moreover, the ^{13}C NMR spectra data of C-21 (δ_C 76.4), C-23 (δ_C 21.4), C-24 (δ_C 53.4) and C-25 (δ_C 70.4) for compound **1** (in DMSO-d_6, Table 1) were in good agreement with those reported for 3β,12β,20*S*,21β,25-pentahydroxy-21,24*R*-cyclodammarane 3-*O*-α-L-rhamnopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→3)]-α-L-arabinopyranoside [9] (in DMSO-d_6) at 76.1 (C-21), 21.1 (C-23), 53.0 (C-24) and 70.4 (C-25), suggesting the same configuration at C-21 and C-24. On the basis of the above evidences, the structure of compound **1** was deduced to be (20*S*, 24*R*)3β,20,21β,25-tetrahydroxy-21,24-cyclodammarane.

Compound **2** was obtained as white amorphous powder. $[\alpha]_D^{20}$ +5.54 (*c* 0.73, CH_3COCH_3). Its molecular formula, $C_{23}H_{38}O_3$, was deduced from the HR-TOF-MS (*m/z* 385.2715 $[M+Na]^+$, Calcd. for $C_{23}H_{38}O_3Na$ 385.2713), The IR spectrum showed absorption bands for hydroxyl group at 3415 cm^{-1}, carboxyl group at 1708 cm^{-1}. The ^{1}H NMR