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A New Triterpenoid from "*Gualou-xiebai-baijiu-tang*" Consisting of *Fructus trichosanthis* and *Bulbus allii macrostemi*

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Abstract: A new triterpenoid saponin was isolated by bioactivity-guided isolation from "Gualou-xiebai-baijiu-tang" consisting of *Fructus trichosanthisi* and Bulbus *allii macrostemi*. Its structure was determined as 3-O-β-D-galactopyranosyl–hederagenin 28-O-β-D-xylopyranosyl (1→6)- β-D-galactopyranosyl ester by means of chemical evidences and spectral analysis.

Keywords: "Gualou-xiebai-baijiu-tang", triterpenoid saponin**,** 3-O-β-D-galactopyranosylhederag-enin 28-O- -D-xylopyranosyl (1→6)- β-D-galactopyranosyl ester.

"Gualou-xiebai-baijiu-tang" is a well-known classic recipe in traditional Chinese medicine, which is alcoholic extracted and consists of *Fructus trichosanthis* and *Bulbus allii macrostemi*. It has been used for the treatment of coronary heart disease and angina pectoris[1]. So far research on this prescription was focused on its pharmacological activities and the chemical constituents of *Trichosanthes kirilowii* Maxim. and *Allium macrostemon* Bge.[2, 3]. There is no report on the effective principles of this prescription yet. In this paper, we will introduce the elucidation of a new triterpenoid isolated from the active part of this prescription.

Compound **1**, a colorless amorphous powder, mp 276~277°C, showed a quasimolecular ion peak at *m/z* 951$[M+Na]^+$ in the positive FAB-MS. A molecular formula of $C_{47}H_{76}O_{18}$ can be determined by FAB-MS as well as from ^{13}C and ^1H-NMR data. The IR spectrum showed the presence of an ester carbonyl group at 1724.0 cm^{-1} and an olefinic group at 1629.6 cm^{-1}.

The ^1H-NMR spectrum revealed signals due to six tertiary methyl groups (δ 0.87, 0.88, 0.94, 0.99, 1.13, 1.18), one trisubstituted olefinic proton (δ 5.42, t, J=3.0Hz) and three anomeric protons (δ 4.98, 5.03 and 6.25). The ^{13}C-NMR spectrum showed signals of a pair of olefinic carbons at 122.9 and 144.2, three anomeric carbons at 95.7, 105.3 and 106.6, and a carbonyl carbon at 176.6. All these data suggested that compound **1** was a triterpenoid saponin related to oleanic acid. Comparison of the signals from the aglycone of **1** in the ^{13}C-NMR spectrum with the literature[4] showed that the aglycone of **1** was hederagenin.

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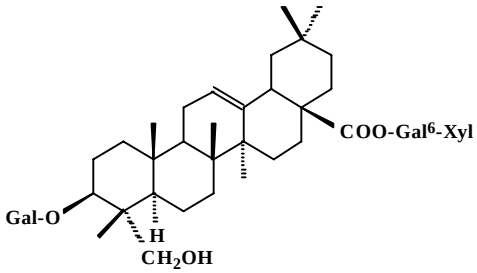
Figure 1 The structure of compound **1**



On acid hydrolysis, xylose and galactose were identified by co-chromatography on HPTLC with authentic samples. Hydrolysis of **1** with ammonia at room temperature for 10 h, xylose and galactose were detected by HPTLC. According to FAB-MS fragments, it can be concluded that the ratio of galactose and xylose was 2 to 1. The β-form anomeric configurations for the galactoses and xylose were judged from their $J_{H1,H2}$ coupling constants (J=7.2, 7.8 and 7.8Hz, respectively)[3]. The spin systems for sugars were assigned on the basis of spectroscopic evidences obtained by DQCOSY, HMQC and TOCSY experiments. The sugar linkages were determined on the basis of HMBC spectrum. A cross peak of long-range coupling was observed between a proton signal at 6.25 (Gal-H-1) and a carbonyl signal at 176.6 (C-28), whereas a proton signal at 5.03 (Xyl-H-1′) was correlated with carbon signal at 69.6 (Gal-C-6). The HMBC data suggested that galactose and xylose linked at C-28. A proton signal at 4.98 (Gal-H-1′′) showed a cross peak with carbon signal at 82.0 (C-3) indicating that another galactose linked at C-3. By comparisons of the ^{13}C-NMR spectral data of **1** with those of oleanolic acid[5], the signal of C-3 shifted downfield by approximately +6.0 ppm, while the signals of C-2 and C-4 shifted to up field by –1.0 ppm and –1.6 ppm respectively. The signal of C-28 also shifted to up field by –2.0 ppm. All these evidences indicated that the two sugars of **1** were linked at C-3 and C-28 of oleanolic acid.

The relative configuration of **1** was confirmed by NOESY spectrum. Furthermore, the characteristic ion peaks at *m/z* 929$[M+H]^+$, 796$[M–pentose]^+$, 766$[M–hexose]^+$, 617$[M–pentose–hexose–H_2O+H]^+$, 472$[alycone]^+$ and 437$[aglycone– 2\times H_2O+H]^+$ in the positive ion FAB-MS confirmed the sugar linkages.

From the above evidences, the structure of **1** was elucidated to be 3-O-β-D-galacto pyranosyl-hederagenin28-O-β-D-xylopyranosyl (1→6)-β-D-galactopyranosyl ester.

Table 1 The assignment of carbon signals of compound **1** (δ ppm)

No.	^{13}C	^{1}H	No.	^{13}C	^{1}H
1	38.9	1.57(H, m) 1.04(H, m)	C-3		
			Gal-1	106.6	4.98(H, d, J=7.2Hz)
2	26.1	2.25(H, m) 2.02(H, m)	2	71.0	4.27(H, m)
3	82.0	4.23(H, m)	3	74.8	4.06(H, m)
4	42.2		4	69.5	4.21(H, m)
5	47.7	1.67(H, m)	5	78.0	4.10(H, m)
6	18.2	1.66(2H, m)	6	62.7	4.47(H,dd, J=11.4,2.4Hz)4.32(H, m)
7	34.0	1.30(H, m), 1.11(H, m)	C-28 Gal-1		
				95.7	6.25(H, d, J=7.8Hz)
8	40.0		2	71.6	4.20(H, m)
9	48.2	1.77(H, m)	3	73.9	4.11(H, m)
10	37.0		4	69.6	4.33(H, m)
11	23.4	1.90(2H, m)	5	78.7	4.21(H, m)
12	122.9	5.42(H. t, J=3.0 Hz)	6	69.6	4.25(2H,m)
13	144.2		Xyl-1	105.3	5.03(H, d, J=7.8Hz)
14	43.5		2	75.2	4.02(H, t, J=8.4Hz)
15	28.3	2.30(H, m) 1.08(H, m)	3	78.4	3088(H, m)
16	23.7	1.98(2H, m)	4	71.0	4.28(H, m)
17	47.0		5	67.0	4.27(H, m) 3.73(H, d, J=10.8Hz)
18	41.7	3.19(H,dd, J=13.8, 4.2Hz)			
19	46.2	1.71(H, m)			
		1.22(H, dd, J=13.8,)			
20	30.7				
21	32.9	1.61(H, m) 1.30(H, m)			
22	32.6	1.88(H, m) 1.75(H, m)			
23	64.6	4.21(H, m) 3.70(H, m)			
24	13.6	0.94(3H, s)			
25	16.3	0.99(3H, s)			
26	17.6	1.13(3H, s)			
27	26.1	1.18(3H, s)			
28	176.6				
29	23.1	0.88(3H, s)			
30	23.9	0.87(3H, s)			

Notes: 1. All spectra were recorded on INOVA 600 MHz NMR spectrometer in Pyridine-d_5
2. The signals of carbon and proton were unambiguously assigned through HMQC, DQCOSY, TOCSY and HMBC.

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