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Two New Compounds from *Hemsleya penxianensis* var. *gulinensis*

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Abstract: Two new compounds, oleanolic acid 28-O-β-D-glucopyranosyl-3-O-α-L-arabinopyranosyl-(1→3)-(6′-butyl ester)-β-D-glucuropyranoside **1**, oleanolic acid 28-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside **2** have been isolated from the roots of *Hemsleya penxianensis* var. *gulinensis*. Their structures were determined on the bases of the spectral and chemical evidences.

Keywords: *Hemsleya penxianensis* var. *gulinensis*, cucurbitaceae, oleanolic acid 28-O-β-D-glucop -yranosyl-3-O-α-L-arabinopyranosyl-(1→3)-(6′-butyl ester)-β-D-glucuropyranoside, oleanolic acid 28-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside.

The plant resources of the genus *Hemsleya* (Curcubitaceae) are abundant in Yunnan and Sichuan provinces. Most of the plants from the genus grow in the subtropical region at altitudes about 1500-2000 meters. The plants are used as herb medicines, which could cure bronchitis, bacillary dysentery, and tuberculosis. The compound from this genus was not reported in previous literature. In this paper, we report the structural elucidation of the new compounds **1** and **2**.

4 kg of methanol extract of the roots of *Hemsleya penxianensis* var. *gulinensis* was evaporated *in vacuo*. The residue was solved in water, and then extracted with *n*-butanol. The 325 g *n*-butanol extract was fractionated on D-101, eluted with EtOH-H_2O(50%). The fractions was repeatedly chromatographed on silica gel column, eluted with $CHCl_3$:CH_3OH:H_2O (8:3:0.3) to give the compounds **1** and **2**.

Compound **1** was a white powder. Its molecular formula was determined as $C_{51}H_{82}O_{18}$ by access FAB-MS(neg.) at *m/z* 981.4269, and the unsaturation is eleven. The FAB-MS also displayed $[M\text{-}1\text{-}162]^-$(100), $[M\text{-}1\text{-}162\text{-}132]^-$, $[M\text{-}1\text{-}162\text{-}132\text{-}232]^-$, which showed that it may include one six-carbon glycoside and one five-carbon glycoside.

The IR spectrum (KBr) displayed absorption bands for the groups hydroxyl (3443 cm^{-1}), carbonyl (1740 cm^{-1}), double bond (1650 cm^{-1}), and ester (1075 cm^{-1}).

The ^{13}C NMR and DEPT spectra of **1** displayed 51 carbon signals including eight methyl, fifteen methylene, nineteen methine and nine quarternary carbons. The ^{13}C and ^1H NMR showed the presence of carbonyls at δc 177.98 and 170.56, the signal of double bond at δc 144.88 (C), δc 123.72 (CH) and δ_H 5.32 (1H, C-12). The spectra also

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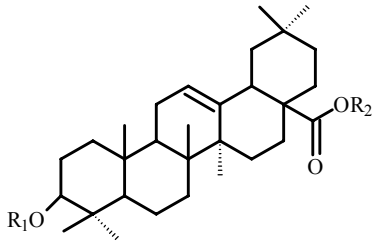
showed the presence of hydroxyl at δc 110.93-62.53 and δ_H 6.28-3.21 further indicating the presence of the glycoside.

On alkaline hydrolysis, **1** yielded glucose which was identical with $[M-1-162]^-$ in FAB-MS and that suggested that its 28 position had glucosyl ester. On acid hydrolysis, **1** yielded glucuronic acid, glucose and arabinose. From the $CHCl_3$ extract of acid hydrolyzate, a white powder was obtained, which was identical with oleanolic acid by PC comparition with authentic sample. The 2D NMR (HMQC) and ^1H NMR spectra showed δ_H 6.28 (d, 1H, *J*=7.32Hz), 5.31(d, 1H, *J*=7.04Hz) and 4.94 (d, 1H, *J*=7.8Hz), which indicated that glucopyranosyl, glucuropyranosyl, and arabinopyranosyl are in the β, β, and α conformations, respectively. The ^{13}C NMR spectra showed the signal of hydroxyl at δc 86.38, indicating the presence of 3-O-α-L-arabinopyranosyl-(1→3)-β-D-glucuropyranoside. The spectra was identical with those of oleanolic acid 28-O-β-D glucopyranosyl-3-O-α-L-arabinopyranosyl-(1→3)- β-D-glucuropyranoside (3) expect for the signal at δc 66.18 (CH_2), 31.7(CH_2), 18.94 (CH_2), 14.09(CH_3) in the ^{13}C NMR and $[M_1-M_3=56]$ in FAB-MS spectrum suggesting that compound **1** had the same skeleton and substitutied groups as compound **3**. These results led to the structural information of compound **1** as oleanolic acid 28-O-β-D-glucopyranosyl -3-O-α-L-arabinopyranosyl-(1→3)-(6′-butyl ester)- β-D-glucuropyranoside. The data of ^{13}C NMR spectra was displayed on **Table 1**.

Figure 1 Structure of **1** and **2**



1 R_1= – glcUA$^{3\to1}$ara R_2= – glc

2 R_1= H R_2= – glc$^{6\to1}$glc

Compound **2** was obtained as white crystals. Its access FAB-MS (neg.) gave molecular ion $[M-1]^-$ at 779.2969, which fits the molecular formula $C_{42}H_{68}O_{13}$, and also showed $[M-1-162]^-$, $[M-1-162-162]^-$ (100), which indicated the presence of glycoside.

The IR spectrua (KBr) displayed absorption bands for the groups hydroxyl (3644 cm^{-1}), carbonyl (1725 cm^{-1}), double bond (1638 cm^{-1}), and ester (1071 cm^{-1}).

The ^{13}C NMR and DEPT spectra displayed forteen signals including seven methyl, twelve methylene, fifteen methine, and eight quarternary carbons. The spectra also showed the presence of carbonyl at δ 178.14, and the signals of double bond δc 144.93 (C), δc 123.83(CH) and δ_H 5.32 (t, 1H, C-12). The signals of hydroxyl group at δc 104.70-62.79 and δ_H 5.41-3.21 in ^{13}C and ^1H NMR indicated that **2** contented glycoside.

The presence of hydroxyl at δc 79.84(CH, C-3) indicated that the C-3 position had not formed ester with glycoside.

On alkaline hydrolysis, compound **2** yield only glucose, which was identical with $[M-1-162]^-$ and $[M-1-162-162]^-$ in FAB-MS. We concentrated the solution *in vacuo* and extracted it with $CHCl_3$ three times. We got white powder which was determined as oleanolic acid by comparing with authentic sample. The ^1H NMR spectra showed δ_H 4.41(d, 1H, *J*=8.12Hz) and δ_H 5.41(d, 1H, *J*=7.82Hz), which indicated that two glucopyranosyl groups are in β conformation. The 2D NMR spectra data suggested that one glucopyranosyl (C-6) is linked with the (C-1) glucopyranosyl.

From these chemical and spectral data, the structure of compound **2** is confirmed to be oleanolic acid 28-O-β-D-glucopyranosyl-(1→6)- β-D-glucopyranoside. The data of the ^{13}C NMR spectra of compound **1**, **2** were displayed on **Table 1**.

Table 1 ^{13}C NMR (125 MHz) data of **1**,**2** in CD_3OD (δ ppm)

position	**1**	**2**			**1**	**2**
1	40.17	39.87	3-O-glcUA	1′	105.58	
2	26.70	28.87		2′	74.07	
3	91.28	79.78		3′	86.38	
4	40.84	40.67		4′	72.86	
5	57.15	56.84		5′	76.30	
6	17.75	17.87		6′	170.56	
7	33.54	33.52	$COOCH_2CH_2CH_2CH_3$	α	66.18	
8	40.83	40.64	$COOCH_2CH_2CH_2CH_3$	β	31.70	
9	47.98	47.90	$COOCH_2CH_2CH_2CH_3$	γ	18.94	
10	37.89	38.22	$COOCH_2CH_2CH_2CH_3$	δ	14.09	
11	24.02	24.48	ara (1→3)	1′	106.78	
12	123.72	123.83		2′	71.48	
13	144.88	144.93		3′	74.61	
14	42.60	42.79		4′	69.65	
15	28.83	28.86		5′	67.34	
16	24.02	24.48	28-O-glc	1′	95.67	95.80
17	47.18	47.20		2′	73.86	74.00
18	42.80	42.60		3′	78.96	75.17
19	47.18	47.10		4′	71.10	71.03
20	31.54	31.62		5′	78.60	78.09
21	34.50	34.92		6′	62.53	69.53
22	33.14	33.92	glc (1→6)	1′		104.70
23	28.58	28.78		2′		77.86
24	17.01	16.35		3′		78.04
25	16.06	16.08		4′		71.61
26	17.75	17.87		5′		78.24
27	26.47	26.32		6′		62.79
28	177.98	178.14				
29	33.54	33.52				
30	24.03	24.08				

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