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A novel triterpenoid saponin from bulbs of *Bolbostemma paniculatum*

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Abstract: Objective To study the triterpenoid saponin from bulbs of *Bolbostemma paniculatum*. **Methods** The compound was isolated by repeated silica gel chromatographies and its strcuture was elucidated on the basis of physico chemical property and spectral analysis. **Results** A novel triterpenoid saponin was isolated and determined as olean 12-en-28-oic acid, 3-{[2-*O*-[6-*O*-[(3R)-4-carboxy-3-hydroxy-3-methyl-1-oxobutyl]-β-*D*-glucopyranosyl]-β-*D*-glucopyranosyl] oxy}-2, 16, 23-trihydroxy-28-[2-*O*-α-*L*-rhamnose (1→2)-α-*L*-arabinopyranosyl] ester (Ⅰ). **Conclusion** Compound Ⅰ is a novel compound named as dexylosyltubeimoside Ⅲ.

Key words: *Bolbostemma paniculatum* (Maxim.) Franquet; triterpenoid saponin; dexylosyltubeimoside Ⅲ

土贝母中一个新的三萜皂苷

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摘 要: 目的 对土贝母 *Bolbostemma paniculatum* 的三萜皂苷成分进行分离和结构鉴定。**方法** 采用反复柱色谱方法进行分离, 通过理化性质和波谱分析鉴定结构。**结果** 从土贝母中分离并鉴定了 1 个新的三萜皂苷脱木糖土贝母苷丙(dexylosyltubeimoside Ⅲ)。**结论** 化合物Ⅰ为新化合物。

关键词: 土贝母; 三萜皂苷; dexylosyltubeimoside Ⅲ

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The bulbs of *Bolbostemma paniculatum* (Maxim.) Franquet is a Chinese folk medicine named as "Tu Bei Mu". Tubeimosides Ⅰ, Ⅱ, and Ⅲ, isolated from the folk medicine, showed significant antitumor, anti-inflammatory, and antitumor-promoting effects[1-3]. Recent studies have reported the isolation and structural elucidation of nine new triterpenoid saponin from *B. paniculatum*, which has antiviral activity[4]. The isolation of a novel cyclic bisdesmoside, dexylosyltubeimoside Ⅲ, from the ethanol extracts of the bulbs of *B. paniculatum* has been reported here.

1 Apparatus and materials

The optical rotations were measured on a Perkin-Elmer 241 polarimeter. Melting points of the compound was determined with an XT-4A apparatus. IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. NMR spectra were measured with a Bruker DRX-500 spectrophotometer. A YG-20 250 mass spectrometer

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was used to record the MS data. Silica gel (200—300 meshes) and silica gel GF_{254} (Qingdao Marine Chemical Group Co.) were used for column chromatography and TLC, respectively.

B. paniculatum was collected from Jiangxian, Shanxi Province, China, in December 2003, and identified by Prof. Tu Pengfei (School of Pharmaceutical Sciences, Health Science Center, Peking University). A voucher specimen was deposited in the Modern Research Center of Traditional Chinese Medicine, Peking University.

2 Extraction and isolation

B. paniculatum (20 kg) was milled and extracted three times with 95% EtOH for 2 h each time, and the solvent was removed under reduced pressure. The 95% ethanol extract was suspended in water and was partitioned with petroleum ether, EtOAc and *n*-BuOH. The *n*-butanol fraction was chromatographed on D-101 macroporous resin, eluting successively with water, 10%, 30%, 50%, 70%, and finally 95% EtOH. The 50% EtOH fraction was repeated column chromatography on silica gel ($CHCl_3$-CH_3OH-H_2O, 65 : 35 : 10), Sephadex LH-20 (70% MeOH) and HPLC (50% MeOH) to afford dexylosyltubeimoside Ⅱ.

3 Identification

Compound Ⅰ: a white amorphous powder, mp 200—202 ℃, $[\alpha]_D^{20}$ +15 (C 0.56, MeOH), has a molecular formula $C_{59}H_{92}O_{27}$ determined from its ESI-MS (*m/z* 1 250 $[M+NH_4]^+$) and NMR data. Its IR absorption bands at 3 415 (OH), 1 734 (C=O), 1 675 (C=C), 1 454 and 1 382 were observed. The ^{1}H-NMR spectrum suggested the presence of six singlet methyls (δ: 0.89, 0.95, 1.14, 1.29, 1.53 and 1.85), one olefinic proton at δ 5.56 (H-12) and four anomeric proton signals [δ 5.00 (d, J=7.5 Hz, H-1 of Glc Ⅰ), 5.26 (d, J=7.5 Hz, H-1 of Glc Ⅱ), 5.86 (d, J=7.8 Hz, H-1 of Ara), 6.33 (brs, H-1 of Rha), which correlated in the HMQC spectrum with δ (C) 103.1 (C-1 of Glc Ⅰ), 105.7 (C-1 of Glc Ⅱ), 94.7 (C-1 of Ara), 102.5 (C-1 of Rha)]. A comparison of the NMR data of Ⅰ with that of tubeimoside Ⅲ showed that compound Ⅰ was lack of a set of data of xylose moiety. Acid hydrolysis of Ⅰ produced glucose, arabinose, rhamnose by TLC comparison with authentic samples. All proton and carbon signals in the NMR spectra (Table 1) were assigned by ^{1}H-^{1}H COSY, TOCSY, HMBC, and HMQC spectra.

Table 1 ^{1}H-NMR (500 MHZ) and ^{13}C-NMR (125 MHz) Data of compound Ⅰ in C_5D_5N

Position	C	H	Position	C	H
1	44.1	2.18 m, 1.26 m	Glc(Ⅰ)		
2	70.0	4.72 m	1	103.1	5.00 d (7.5)
3	83.1	4.16 m	2	84.8	4.03 m
4	42.3		3	78.3	4.12 m
5	47.6	1.76 m	4	70.6	4.07 m
6	18.4	2.18 m, 1.68 m	5	78.1	3.78 m
7	33.1	1.95 m, 1.76 m	6	62.3	4.35 m, 4.21 m
8	40.2		Glc(Ⅱ)		
9	47.6	2.03 m	1	105.7	5.26 d (7.5)
10	37.0		2	76.9	4.05 m
11	24.0	2.33 m, 2.05 m	3	77.4	4.08 m
12	122.8	5.56 m	4	70.6	4.11 m
13	144.6		5	75.7	3.98 m
14	42.0		6	64.1	4.63 m, 4.11 m
15	36.8	2.24 m, 1.85 m	Ara		
16	73.4		1	94.7	5.86 d (7.8)
17	49.1		2	76.4	4.63 m
18	40.9	3.50 m	3	72.4	4.07 m
19	46.5	1.80 m, 1.33 m	4	69.8	4.05 m
20	30.7		5	67.7	4.19 m, 3.76 m
21	35.9	2.37 m, 1.24 m	Rha		
22	32.4	2.33 m, 2.18 m	1	102.5	6.33 brs
23	64.5	4.38 m, 3.78 m	2	72.4	4.89 brs
24	15.2	1.29 s	3	73.4	4.21 m
25	17.4	1.53 s	4	75.7	5.83 t (9.6)
26	17.5	1.14 s	5	67.9	4.49 dd (9.6, 3.0)
27	27.3	1.85 s	6	18.21	1.37 d (6.0)
28	175.6				
29	33.1	0.89 s			
30	24.3	0.95 s			
Acyl moiety					
1′	171.6				
2′	47.1	3.36 d (14.1), 2.77 d (14.1)			
3′	70.5				
4′	46.5	3.10 d (16.8), 2.65 d (16.8)			
5′	171.8				
6′	26.3	1.62 s			

The linkages between sugars and aglycone were decided mainly by HMBC spectra (Fig. 1).

In the HMBC spectrum, long-range correlations were observed between the anomeric proton signal at δ 5.00 (H-1 of Glc Ⅰ) and the carbon signal at δ 83.1 due to the C-3 of aglycone, the anomeric proton signal at δ 5.26 (H-1 of Glc Ⅱ)

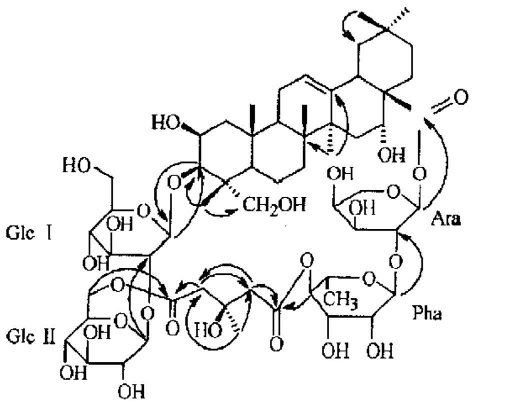

Fig. 1 Structure and main HMBC of compound Ⅰ (H→C)

and the carbon signal at δ 84.8 due to the C-2 of Glc Ⅰ, the anomeric proton signal at δ 5.86 (H-1 of Ara) and the carbon signal at δ 175.6 due to the C-28 of aglycone, the anomeric proton signal at δ 6.33 (H-1 of Rha) and the carbon signal at δ 76.4 due to the C-2 of Ara, the carbon signal at δ 171.6 (C-1 of HMG) and the proton signals at δ 4.63 and δ 4.11 (H-6a and 6b of Glc Ⅱ), the carbon signal at δ 171.8 (C-5 of HMG) and the proton signal at δ 5.83 (H-4 of Rha). From these data, the structure of compound Ⅰ was elucidated as dexylosyltubeimoside Ⅲ.

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三列凹顶藻中倍半萜成分的研究

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摘 要: 目的 从三列凹顶藻 *Laurencia tristicha* 中寻找具有多样性结构的倍半萜化学成分, 供药理活性筛选。**方法** 采用凝胶柱色谱、硅胶柱色谱、重结晶和高效液相色谱等方法进行分离; 借助包括一维和二维 NMR 等波谱方法和 X-单晶衍射鉴定化合物的结构; 用 MTT 法对得到的化合物进行细胞毒活性评价。**结果** 分离得到 5 个倍半萜类化合物, 分别鉴定为海兔阿普里素(aplysin, Ⅰ)、海兔阿普里醇(aplysinol, Ⅱ)、去溴海兔阿普里醇(debromoaplysinol, Ⅲ)、凹顶藻联苯(laurebiphenyl, Ⅳ)、约翰斯顿醇(johnstonol, Ⅴ); 在人肿瘤细胞株 HCT-8、Bel-7402、BGc-823、A549 和 HeLa 模型上, 化合物Ⅳ对所有细胞株均显示毒性, 化合物Ⅲ对 HeLa 细胞显示中等强度的细胞毒活性, 其他化合物对所有细胞株均无明显毒性, IC_{50} 均大于 10.0 μg/mL。**结论** 化合物Ⅰ～Ⅴ均为首次从三列凹顶藻中得到, 化合物Ⅲ对 HeLa 细胞具有中等强度的选择性细胞毒活性, 化合物Ⅳ对所有细胞株均显示毒性。

关键词: 三列凹顶藻; 倍半萜; 细胞毒活性

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Sesquiterpene components of *Laurencia tristicha*

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