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狗筋蔓中的植物蜕皮甾酮类化合物

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摘要: 从我国民间草药狗筋蔓(*Cucubalus baccifer* L.)全草的乙醇提取物的正丁醇萃取部分分离得到6个化合物, 通过波谱及化学方法鉴定了它们的结构, 分别为 ecdysterone (**1**), 24(28)_ecdysterone (**2**), 22_deoxyecdysterone (**3**), 25_hydroxypanuosterone (**4**), rubrosterone (**5**), 2,22_dideoxyecdysterone 3β_O_β_*D*_glucopyranoside (**6**)。其中化合物**6**为新化合物; 化合物**1**~**5**为首次从该植物中分得。

关键词: 石竹科; 狗筋蔓; 植物蜕皮甾酮; 2,22_dideoxyecdysterone 3β_O_β_*D*_glucopyranoside
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Phytoecdysterones from *Cucubalus baccifer* (Caryophyllaceae)

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Abstract: Six phytoecdysterones have been isolated from the *n*_BuOH portion of *Cucubalus baccifer* L., a Chinese folk medicinal plant. Their structures were elucidated as ecdysterone (**1**), 24(28)_ecdysterone (**2**), 22_deoxyecdysterone (**3**), 25_hydroxypanuosterone (**4**), rubrosterone (**5**) and 2,22_dideoxyecdysterone 3β_O_β_*D*_glucopyranoside (**6**) respectively on the basis of spectroscopic and chemical methods. Among them compound **6** was a new phytoecdysterone glycoside and **1**– **5** were first obtained from this plant.

Key words: Caryophyllaceae; *Cucubalus baccifer*; phytoecdysterones; 2,22_dideoxyecdysterone 3β_O_β_*D*_glucopyranoside

Cucubalus baccifer L. is a Chinese folk herb used for arthritis, pulmonary tuberculosis (in oral) and scrofula (topical use)[1]. It is sporadically distributed in northeast, northwest and southwest of China as well as in Europe, the middle of Asia and India[2]. From the *n*_BuOH portion of the whole plants six phytoecdysterones were isolated. Their structures were characterized as ecdysterone (**1**), 24(28)_ecdysterone (**2**), 22_deoxyecdysterone (**3**), 25_hydroxypanuosterone (**4**), rubrosterone (**5**), 2,22_dideoxyecdysterone 3β_O_β_*D*_glucopyranoside (**6**) respectively by means of spectroscopic and chemical methods. Compound **6** was a new phytoecdysterone glycoside and **1**– **5** were isolated from this plant for the first time.

1 Results and Discussion

Compound **6** was isolated as a colorless gum. Its composition of $C_{33}H_{54}O_{10}$ was derived from the combination of ^{13}C_NMR, DEPT and negative FAB_MS at m/z 609 $[M-H]^-$. The DEPT spectra revealed five methyls, eleven methelenes, ten methines and seven quaternary carbons. The five methines of δ 71.78– 77.84 and δ 102.90 and one methelene of δ 62.87 suggested the presence of one sugar moiety. It was further proved to be a glucose by TLC comparison with authentic sample after acidic hydrolysis. The IR absorptions at 3 348 and 1 653 cm^{-1} were indicative of hydroxyl group and conjugated carbonyl functionality respectively. The UV spectrum at maximum band of 244 nm suggested the partial structure of 7_en_6_one. The evidence mentioned above suggested that **6** was a phytoecdysterone glycoside. The ^{13}C_NMR data of B, C and D ring of **6** was identical with that of pinnatasterone[3]. At the same time, the ^{13}C_NMR data of A ring of **6** was in agreement with that of blechnoside A[4]. Thus the aglycone of **6** was identified as 2,22_dideoxyecdysterone. The glycosidation shift of C_3 suggested that glucosyl was linked with 3β_OH. The β_configuration of glycoside bond was determined by coupling constant of anomeric proton (δ 4.35, d, J = 7.8 Hz). Hereby the structure of **6** was determined to be 2,22_dideoxyecdysterone 3β_O_β_*D*_glucopyranoside.

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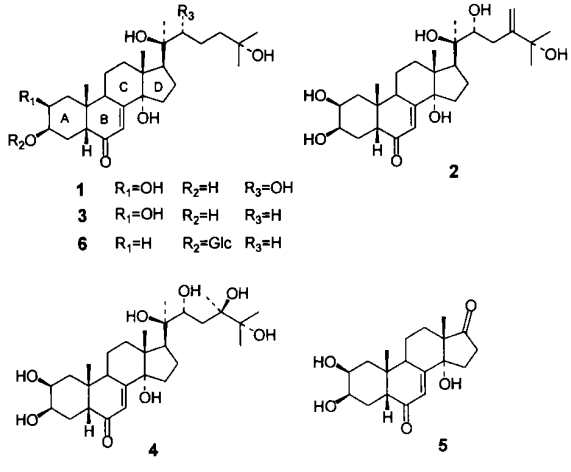
Five known compounds ecdysterone (**1**)[5], 24(28)-ecdysterone (**2**)[6], 22-deoxyecdysterone (**3**)[7], 25-hydroxypanuosterone (**4**)[8], rubrosterone (**5**)[9] were also isolated. Their structures were identified on the basis of their physical constants and spectral data. All of them were isolated from this plant for the first time.

Table 1 ^{13}C-NMR data of compounds **1**–**6**

Carbon	1	2	3	4	5	6
1	38.71	39.28	37.43	37.60	37.87	30.19
2	68.12	68.52	68.71	68.71	68.09	27.93
3	68.18	68.72	68.53	68.52	68.09	71.48
4	32.47	32.51	32.82	32.75	32.48	31.49
5	51.43	51.80	53.42	50.56	51.60	53.44
6	203.44	206.46	206.43	206.39	203.40	206.30
7	121.72	122.16	122.07	121.96	122.14	121.91
8	166.06	167.9	168.07	168.42	163.04	168.97
9	34.53	34.61	35.09	35.14	35.22	*
10	38.05	37.20	39.27	39.26	38.91	37.49
11	21.53	21.55	21.98	21.57	20.26	22.03
12	31.81	31.78	31.58	32.51	33.75	32.57
13	48.17	48.49	48.09	48.58	53.40	48.58
14	84.27	85.28	85.53	85.45	79.68	85.71
15	32.07	32.85	32.39	31.78	29.04	32.57
16	21.19	21.55	21.53	21.06	24.79	20.08
17	50.17	50.49	51.78	50.42	217.37	*
18	17.92	18.05	18.13	18.05	17.33	18.12
19	24.50	24.40	26.50	24.38	24.59	24.24
20	77.62	77.81	75.98	77.92		75.99
21	21.73	21.55	24.40	21.06		26.49
22	76.93	78.01	45.50	73.82		45.70
23	27.52	34.61	20.08	39.26		20.08
24	42.66	155.32	45.50	75.02		45.88
25	69.63	73.62	71.47	77.92		71.48
26	30.06	31.78	29.15	25.96		29.34
27	30.13	32.51	29.35	25.59		29.15
28		110.38		21.57		

* , unobserved signals.



2 Experimental

2.1 General experimental procedures

Melting points were measured from a XRC-1 apparatus and uncorrected. UV spectra were determined with a UV210A spectrometer. IR spectrum was obtained from a Bio-Rad FTS-135 spectrometer with KBr discus. Optical rotation was determined with a JASCO-20C digital polarimeter. MS spectra were recorded from a VG Auto Spec-3000 spectrometer and NMR spectra from a Bruker AM-400 spectrometer.

2.2 Plant materials

Cucubalus baccifer L. was collected at Chenggong County, Yunnan Province, China, in September, 1999. A voucher specimen was kept in the herbarium of Kunming Institute of Botany, The Chinese Academy of Sciences.

2.3 Extraction and isolation

The air-dried powdered whole herbs of *C. baccifer* (24.0 kg) were extracted with 95% ethanol under reflux for three times (2 h, 1 h and 1 h, respectively). The combined extract was concentrated under reduced pressure to furnish the residue which was suspended in water and extracted with petroleum ether (60–90 ℃), EtOAc and n-BuOH successively. The n-BuOH portion was evaporated to dryness to afford the fraction (70.0 g) which was desugarized on D 101 macroporous resin eluted with aqueous MeOH (0∶1–7∶3). The 70% MeOH eluate (20.0 g) was successively subjected to CC over Si gel (200–300 mesh) eluted with gradient $CHCl_3$-MeOH to afford fractions 1 and 2. Fraction 1 was chromatographed over Si gel using $CHCl_3$-MeOH as the eluant to furnish **1** (343 mg). Fraction 2 was subjected to CC over Sephadex LH-20, RP-18 and MCI-gel CHP 20P eluted with MeOH-H_2O (45%–70%) to afford **2** (10 mg), **3** (10 mg), **4** (13 mg), **5** (67 mg) and **6** (10 mg).

2.4 Acidic hydrolysis of 6

A solution of compound **6** (2 mg) in 3 mL methanol and 3 mL HCl was refluxed over a water bath for 3 h. The mixture was performed on TLC and PC respectively. TLC using $CHCl_3$-MeOH-H_2O (3∶2∶0.3) gave the same R_f value (0.6) as glucose, while PC (Whatman No. 1) developed with *n*-BuOH-HOAc-H_2O (4∶1∶5, upper layer) displayed the same R_f value as glucose at 0.3.

2.5 Identification

Compound 6 $C_{33}H_{54}O_{10}$, colorless gum, $[\alpha]_D^{28}$ = + 49° (*c* 1.1, in MeOH). IR (cm^{-1}): 3348 (hydroxyl), 1653 (conjugated carbonyl). UV (nm): 244 (conjugated carbonyl). neg. FAB-MS: 609 $[M-H]^-$

(100), 447 [M - 163]$^-$ (12). ^{1}H_NMR (CD_3OD) δ: 0.84 (3H, s, H_19), 0.94 (3H, s, H_18), 1.18 (6H, s, H_26 and H_27), 1.24 (3H, s, H_21), 3.85 (1H, d, J = 1.7 Hz, H_3), 5.80 (1H, d, J = 1.8 Hz, H_7), 4.35 (1H, d, J = 7.8 Hz, H_1′); ^{13}C_NMR data see Table 1.

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