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黄棉木中两个新的三萜类化合物*

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摘要：从黄棉木（*Metadina trichotoma*（Zoll. et. Mor.）Bakn.）树皮中分离得到2个新的三萜类化合物：3-oxo-29-hydroxy-urs-12-en-27, 28-dioic acid（黄棉木素 A，**1**）和 3-oxo-21β-hydroxy-urs-12-en-27, 28-dioic acid（黄棉木素 B，**2**）。其结构主要通过 MS，1D 以及 2D NMR 等波谱方法鉴定。

关键词：黄棉木；茜草科；三萜；黄棉木素 A；黄棉木素 B
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Two New Triterpenes from *Metadina trichotoma* (Rubiaceae)

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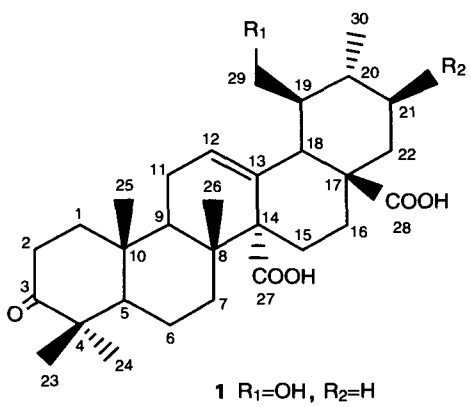
Abstract: Two new triterpenes, 3-oxo-29-hydroxy-urs-12-en-27, 28-dioic acid (Metatrichosin A, **1**) and 3-oxo-21β-hydroxy-urs-12-en-27, 28-dioic acid (Metatrichosin B, **2**), were isolated from the barks of *Metadina trichotoma* (Zoll. et. Mor.) Bakn. Their structures were mainly determined by MS, 1D and 2D NMR spectroscopic methods.

Key words: *Metadina trichotoma*; Rubiaceae; Triterpenes; Metatrichosin A; Metatrichosin B

Metadina trichotoma (Zoll. et. Mor.) Bakn. belongs to the Rubiaceae and is a unique species in the genus *Metadina*, which is distributed in Southwest of China, Vietnam, and India etc. (Delectis Florae Reipublicae Popularis Sinicae Agendae Academiae Sinicae Edita, 1999). Up to now, there is no any report on its chemical constituents. We found its methanol extracts showed inhibitory activity on cathepsin B (IC_{50} = 0.77 μg/ml) in our random screening on the crude extracts of some plants in Yunnan province. In order to seek more novel bioactive compounds, we carried out extensive chemical and biological studies on the barks of *M. trichotoma*. In this paper, we described the isolation and structural elucidation of two new triterpenes (Figure 1) from this plant.



1 R_1=OH, R_2=H
2 R_1=H, R_2=OH

Fig. 1 Structures of compound **1** and **2**

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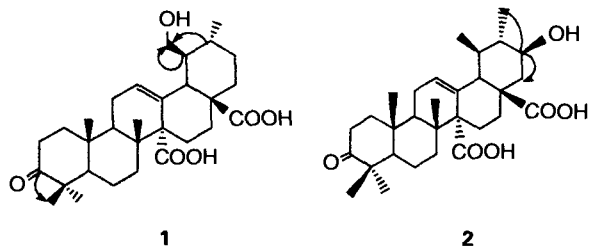
Results and Discussion

Compound **1** was assigned the molecular formula $C_{30}H_{44}O_6$ by HR + TOF-MS at *m/z* 523.3025 [M + Na]$^+$ (calcd. 523.3035), which was confirmed by ^{13}C and DEPT NMR spectra. The ^{13}C and DEPT ^{13}C NMR spectra indicated that **1** may be one triterpene.

The ^{13}C-NMR spectra showed the presence of five Me [δ 27.3 (C-24), 21.7 (C-23), 18.9 (C-30), 17.7 (C-26), 16.6 (C-25)], ten CH_2 [δ 66.2 (C-29), 40.5 (C-1), 37.3 (C-7), 37.2 (C-22), 35.0 (C-2), 26.4 (C-15), 25.7 (C-21), 25.5 (C-16), 24.0 (C-11), 20.7 (C-6)], and six CH [δ 130.5 (C-12), 56.1 (C-5), 55.5 (C-18), 47.8 (C-19), 47.1 (C-9), 32.8 (C-20)], as well as nine quaternary C-atoms [δ 220.7 (C-3), 181.5 (C-28), 178.8 (C-27), 133.9 (C-13), 57.2 (C-14), 49.2 (C-17), 48.3 (C-4), 40.5 (C-8), 37.8 (C-10)]. These data indicated that compound **1** has a urs-12-ene skeleton with a keto group on ring A, and also has five Me and a hydroxymethyl group (Aquino *et al*, 1997). The HMBC spectrum (Figure 2) showed correlations between δ_C 220.7 (C-3) and δ_H 1.02 (3H, s, H-23), which indicated that the C = O was located at C-3. And also the correlations between: δ_C 47.8 (C-19) and δ_H 3.32 (1H, dd, *J* = 7.07, 10.88 Hz, H-29a), δ_C 32.8 (C-20) and δ_H 3.65 (1H, dd, *J* = 3.08, 10.84 Hz, H-29b), which indicated that the OH was located at C-29. So the structure of **1** was determined to be 3-oxo-29-hydroxy-urs-12-en-27, 28-dioic acid, named Metatrichosin A.

Compound **2** was assigned the molecular formula $C_{30}H_{44}O_6$ by HR + TOF-MS at *m/z* 523.3025 [M + Na]$^+$ (calcd. 523.3035), which was confirmed by ^{13}C and DEPT NMR spectra. The ^{13}C and DEPT ^{13}C NMR spectra also indicated that it may be one triterpene. Compared with **1**, compound **2** has one more Me (δ_C 19.1) and CH (δ_C 75.2), and two CH_2 (δ_C 66.2, 25.7) in **1** disappeared, which indicated that the hydroxyl was located at a different position. The HMBC spectrum showed correlations between δ_C 75.2 (C-21) and δ_H 0.86 (3H, d, *J* = 5.96 Hz, H-30), 1.47 (1H, m, H-22a) (Figure 2), which indicated that the hydroxyl was located at C-21. And the ROESY spectrum showed correlation between δ_H 2.22 (1H, d, *J* = 9.15 Hz, H-18) and δ_H 3.73 (1H, dd, *J* = 4.31, 11.96 Hz, H-21), which indicated the OH on C-21 was β configuration (Escudero *et al*, 1985; Piozzi *et al*, 1986). So the structure of **2** was determined to be 3-oxo-21β-hydroxy-urs-12-en-27, 28-dioic acid, named Metatrichosin B.



1 **2**

Fig. 2 HMBC correlation of compound **1** and **2**

Experimental

General ^1H, ^{13}C NMR and 2D NMR spectra were recorded on a Bruker AM-400 or a DRX-500 NMR spectrometer with TMS as internal standard. MS data were obtained on a VG Autospec-3000 spectrometer.

Plant material The barks of *Metadina trichotoma* (Zoll. et. Mor.) Bakn. were collected from Xishuangbanna, Yunnan Province, China in September 2002 and identified by Associate Prof. Wang Hong at Xishuangbanna Tropical Botanical Garden, the Chinese Academy of Sciences.

Extraction and Isolation The dried and powdered barks (9.0 kg) of *M. trichotoma* were extracted with MeOH for three times under room temperature and then concentrated under reduced pressure. The concentrated MeOH extract (1668 g) was dissolved in hot water and extracted with petroleum ether, AcOEt and n-BuOH step by step, and obtained 19 g petroleum ether extract, 85 g AcOEt extract, 780 g n-BuOH extract and 884 g water extract respectively. The AcOEt part was subjected to silica gel column chromatography with $CHCl_3$-MeOH-H_2O (1:0:0 to 8:2.0.2 V/V) and obtained fractions (Fr.) **1**–**8**. Fr. **2** was repeatedly subjected to silica gel column chromatography and eluted with $CHCl_3$/MeOH/H_2O 9:1:0.1 to afford subfractions **1**–**4**, and subfraction **2** was subjected to Sephadex LH-20 column chromatography with $CHCl_3$-MeOH (1:1) to afford **1** (6 mg) and **2** (4 mg).

Metatrichosin A (1), $C_{30}H_{44}O_6$, white solids. $[\alpha]_D^{24}$ = 105.8 (c = 0.20, Acetone). HR + TOF-MS m/z 523.3025 $[M+Na]^+$ (calcd. 523.3035). EI MS m/z 500 $[M]^+$. ^{13}C NMR data see Table 1. ^1H NMR data: 5.61 (1H, brs, H-12), 3.65 (1H, dd, J = 3.08, 10.84 Hz, H-29b), 3.32 (1H, dd, J = 7.07, 10.88 Hz, H-29a), 2.26 (1H, d, J = 11.38 Hz, H-18), 1.02 (3H, s, H-23), 1.02 (3H, s, H-25), 1.00 (3H, s, H-24), 0.90 (3H, d, J = 9.12 Hz, H-30), 0.87 (3H, s, H-26).

Table 1 ^{13}C-NMR data of compound **1** and **2** in CD_3OD

(^{13}C: 100 MHz; δ: ppm)

No.	1	2	No.	1	2
1	40.5 (t)	40.5 (t)	16	25.5 (t)	19.9 (t)
2	35.0 (t)	35.0 (t)	17	49.2 (s)	55.2 (s)
3	220.7 (s)	220.7 (s)	18	55.5 (d)	56.7 (d)
4	48.3 (s)	48.3 (s)	19	47.8 (d)	37.7 (d)
5	56.1 (d)	56.1 (d)	20	32.8 (d)	38.6 (d)
6	20.7 (t)	20.7 (t)	21	25.7 (t)	75.2 (d)
7	37.3 (t)	37.3 (t)	22	37.2 (t)	39.4 (t)
8	40.5 (s)	40.7 (s)	23	21.7 (q)	21.7 (q)
9	47.1 (d)	47.0 (d)	24	27.3 (q)	27.3 (q)
10	37.8 (s)	37.7 (s)	25	16.6 (q)	16.6 (q)
11	24.0 (t)	24.0 (t)	26	17.7 (q)	18.0 (q)
12	130.5 (d)	130.2 (d)	27	178.8 (s)	178.9 (s)
13	133.9 (s)	133.9 (s)	28	181.5 (s)	179.9 (s)
14	57.2 (s)	57.5 (s)	29	66.2 (t)	19.1 (q)
15	26.4 (t)	24.7 (t)	30	18.9 (q)	21.3 (q)

Metatrichosin B (2), $C_{30}H_{44}O_6$, white solids. $[\alpha]_D^{24}$ = 129.7 (c = 0.41, Acetone). HR + TOF-MS m/z 523.3025 $[M+Na]^+$ (calcd. 523.3035). EI MS m/z 500 $[M]^+$. ^{13}C NMR data see Table 1. ^1H NMR data: 5.62 (1H, brs, H-12), 3.73 (1H, dd, J = 4.31, 11.96 Hz, H-21), 2.22 (1H, d, J = 11.15 Hz, H-18), 1.47 (1H, m, H-22a), 1.39 (1H, m, H-22b), 1.04 (3H, s, H-23), 1.04 (3H, s, H-25), 1.02 (3H, s, H-24), 0.95 (3H, d, J = 6.11 Hz, H-29), 0.87 (3H, s, H-26), 0.86 (3H, d, J = 5.96 Hz, H-30).

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