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金黄喇叭菌中一个新的炔酸化合物*

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摘要: 从担子菌金黄喇叭菌 (*Craterellus aureus*) 子实体中分离到3个炔酸类化合物, 其中一个为新化合物, 其化学结构通过波谱学方法和量子化学计算鉴定为 (8*E*, 10*R*, 14*Z*)-10-羟基-8, 14-十八碳二烯-12-炔酸 (**1**)。

关键词: 金黄喇叭菌; 炔酸; 担子菌
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A New Hydroxyl Acetylenic Fatty Acid from the Basidiomycete *Craterellus aureus* (Cantharellaceae)

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Abstract: A new hydroxyl acetylenic acid, named (8*E*, 10*R*, 14*Z*)-10-hydroxy-8, 14-octadecadien-12-ynoic acid (**1**), together with two known compounds (**2**, **3**), were isolated from the ethanol extract of the fruiting bodies of *Craterellus aureus*. Their structures were established by spectroscopic methods (1D- and 2D-NMR experiments). The absolute configuration of **1** was determined to be *R* by computational calculation of optical rotation.

Key words: *Craterellus aureus*; Acetylenic acid; Basidiomycet

The Basidiomycete *Craterellus aureus*, which belongs to the family of Cantharellaceae, is an edible mushroom and widely distributed in China (Huang, 1998). A previous chemical investigation on *Craterellus* sp. led to the isolation of a series of acetylenic acids (Magnus *et al.*, 1989a, b). As one part of our research on bioactive metabolites from higher fungi of Yunnan province, China (Liu, 2005), we investigated the chemical constituents of the fruiting body of *C. aureus* and isolated a new 10-hydroxyl acetylenic acid (**1**), together withtwo known compounds (**2**, **3**). This report described the isolation and structure elucidation of compound **1**, including the determination of the absolute configuration based on computational method.

Results and discussion

Compound **1** was obtained as colorless oil. Its molecular formula was established as $C_{18}H_{28}O_3$ by FAB-MS (neg.), ^{13}C-NMR and DEPT spectra (Table 1), and confirmed by HR-ESI-MS (neg.) m/z 291.1968 ([M-H]$^-$ calcd. for $C_{18}H_{27}O_3$, 291.1960). In the UV spectrum, a strong absorption band at 241 nm indi-

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Table 1 ^{13}C NMR and ^{1}H NMR spectral data for compounds **1** and **2** (in $CDCl_3$)

No	**1**[a]		**2**[b]	
	^{13}C	^{1}H	^{13}C	^{1}H
1	179.2 (s)		180.0 (s)	
2	33.9 (t)	2.34 (t, 7.4 Hz)	34.0 (t)	2.34 (t, 7.4 Hz)
3	24.6 (t)	1.62 (m)	24.6 (t)	1.63 (m)
4	28.6 (t)*	1.25-1.42 (m)	29.0 (t)*	1.31-1.38 (m)
5	28.7 (t)*	1.25-1.42 (m)	29.1 (t)*	1.31-1.38 (m)
6	28.8 (t)*	1.25-1.42 (m)	29.1 (t)*	1.31-1.38 (m)
7	32.0 (t)	2.04 (q, 6.7 Hz)	29.3 (t)*	1.31-1.38 (m)
8	132.9 (d)	5.72 (dt, 15.4, 6.7 Hz)	27.1 (t)	2.05 (m)
9	131.0 (d)	5.55 (dd, 15.4, 6.7 Hz)	131.6 (s)	5.42-5.49 (m)
10	71.1 (d)	4.25 (m)	124.3 (d)	5.42-5.49 (m)
11	28.8 (t)*	2.60 (m)	17.9 (t)	3.08 (m)
12	89.7 (s)		92.4 (s)	
13	79.9 (s)		77.1 (s)	
14	109.1 (d)	5.45 (d, 10.7 Hz)	109.3 (d)	5.42-5.49 (m)
15	143.3 (d)	5.87 (dt, 10.7, 7.4 Hz)	142.7 (d)	5.81 (ddd, 10.7, 7.4, 4.4 Hz)
16	32.2 (t)	2.26 (m)	32.1 (t)	2.26 (dd, 7.4, 4.4 Hz)
17	22.1 (t)	1.42 (m)	22.1 (t)	1.42 (m)
18	13.7 (q)	0.93 (t, 7.4 Hz)	13.7 (q)	0.92 (t, 7.4 Hz)

[a] Data were recorded by Bruker AV-400 (400 100 MHz) and [b] by DRX-500 (500 125 MHz).

* Assignments interchangeable within the same column.

cated the existence of conjugation. The IR absorptions of **1** suggested the presence of a hydroxyl (3 346 cm^{-1}), an acetylene (2 215 cm^{-1}) and a carbonyl (1 711 cm^{-1}) groups. ^{13}C-NMR and DEPT spectra revealed 18 carbon signals for one free carbonyl, two quaternary carbons, four olefinic methines, one oxygenated methine, nine methylenes and one methyl. The HMBC spectrum showed long-range coupling correlations from H-14 (δ_H 5.45, d, J = 10.7 Hz) to C-12 and C-16, H-15 (δ_H 5.87, dt, J = 10.7, 7.4 Hz) to C-13 and C-17, H-16 (δ_H 2.26, m) to C-14 and C-18 (Fig. 2). These data led to the establishment of partial structure A: $C \equiv C\text{-}CH = CH\text{-}CH_2\text{-}CH_2\text{-}CH_3$ (Magnus *et al.*, 1989a, Pang and Sterner, 1991). Analysis of the chemical shift and coupling constants suggested the presence of partial structure B: $CH_2\text{-}CH(OH)\text{-}CH = CH\text{-}CH_2$. The linkage was established by HMBC which demonstrated the following key ^{3}J correlations: from H-3 to C-1, from H-7 to C-9, from H-8 to C-10, from H-9 to C-7 and C-11, from H-10 to C-8 and C-12, from H-11 to C-9 and C-13 (Fig. 2). Therefore, the structure of **1** was determined to be (8*E*, 14*Z*)-10-hydroxy-8, 14-octadecadien-12-ynoic acid (Fig. 1).

Due to the limited amount of compound **1**, we decided to adopt computational method instead of Mosher reactions to determine the absolute configuration. The experimental value of optical rotation for **1** is +25.2 deg, and the calculated det (D) for (*R*)-configuration is +5.3, the calculated k_0 value was 4.8. Since the positive sign of det (D) calculated for (*R*)-1 agreed

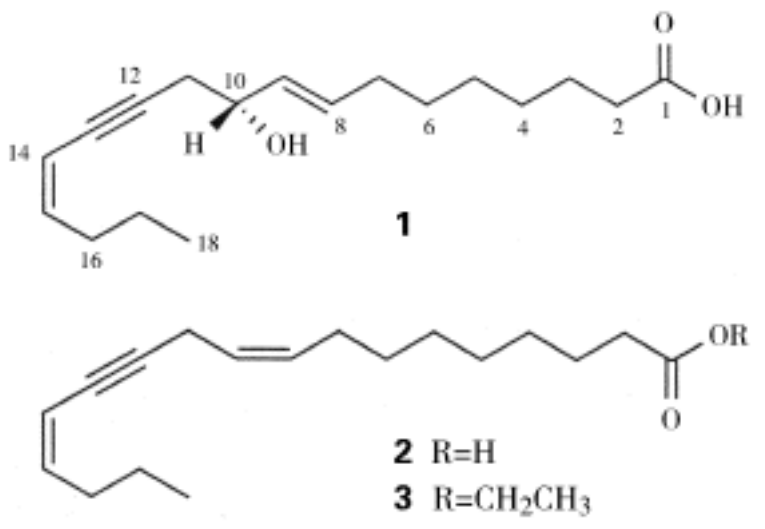

Fig. 1 The structures of compounds **1-3**

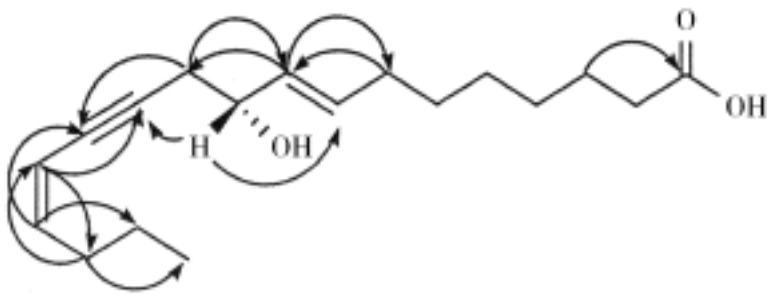

Fig. 2 Selected HMBC correlations for compound **1**

with the recorded positive sign of optical rotation. Thus, the absolute configuration of **1** was assigned as (*R*) (Zhu *et al.*, 2007).

Materials and methods

General Optical rotation was performed on Horiba SEPA-300 digital polarimeter. UV spectrum was recorded on Shimadzu UV-2401 PC spectrophotometer. IR spectrum was obtained on Bruker Tensor-27 spectrometer. ^{1}H- and ^{13}C-NMR spectra were measured on Bruker AV-400 (400/100 MHz) and DRX-500 (500/125 MHz) instruments in $CDCl_3$ with TMS as internal standard. MS was taken on VG Autospec-3000 mass spectrometer and API QSTAR pulsar i spectrometer, in *m/z* (rel. intensities in %). Silica gel (200-300 mesh) (Qingdao Marine Chemical Inc., China) and Sephadex LH-20 (Amersham Biosciences, Sweden) were used for column chromatography.

Fungal Material The fresh fruiting bodies of *C. aureus* were obtained from Tengchong in Yunnan province, China, in August, 2006 and identified by Prof. Zang Mu, Kunming Institute of Botany, Chinese Academy of Sciences (CAS).

Extraction and Isolation The fresh fruiting bodies of *C. aureus* (0.75 kg) were extracted three times with 95% EtOH (5.0 L). After filtration and evaporation in vacuo at 45℃, the residue (34 g) was partitioned between EtOAc and H_2O. The EtOAc layer (14 g) was chromatographed on silica gel, eluted in a step gradient manner with $CHCl_3/CH_3OH$ (1/0 to 1/1) to afford fractions Ⅰ-Ⅴ. Fraction Ⅰ, eluted with $CHCl_3/CH_3OH$ (1/0), was further subjected to column chromatography over silica gel (petroleum ether/EtOAc 100/1) to yield compound **3** (75 mg). Fraction Ⅱ eluted with $CHCl_3/CH_3OH$ (94/6) was submitted to repeated silica gel ($CHCl_3/CH_3OH$ 94/6) to afford six subfractions. Subfractions B and E were followed by Sephadex LH-20 chromatography ($CHCl_3$/MeOH 1/1) to give compounds **2** (20 mg) and **1** (24 mg), respectively.

Compound 1, $C_{18}H_{28}O_3$, Colorless oil; $[\alpha]_D^{20} = +25.2°$ ($c = 0.27$, $CHCl_3$); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 241 (3.72); IR (film) cm^{-1}: 3346, 2958, 2929, 2215, 1711, 1462, 1378; FAB-MS (neg.) *m/z*: 291 $[M-H]^-$; HR-ESI-MS (neg.): 291.1968 ($[M-H]^-$, calcd. 291.1960).

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