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黑盖地花菌中一个新的 grifolin 衍生物

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摘要: 从黑盖地花菌 (*Albatrellus yasuda*) 中分离得到 4 个 grifolin 衍生物: grifolene (1), grifolin (2), grifolic acid (3) 和 neogrifolin (4), 其中 1 为新化合物, 它的化学结构通过波谱学方法鉴定。

关键词: 黑盖地花菌; Grifolin; Grifolene
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A New Grifolin Derivative from the Mushroom *Albatrellus yasuda* (Polyporaceae)

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Abstract: A new grifolin derivative, named grifolene (1), together with grifolin (2), neogrifolin (3) and grifolic acid (4) was isolated from the fruiting bodies of the fungus *Albatrellus yasuda*. The structure of 1 was elucidated on the basis of extensive spectroscopic analysis.

Key words: *Albatrellus yasuda*; Grifolin; Grifolene

The fungus *Albatrellus yasuda* of the family Polyporaceae is mainly distributed in Yunnan, Sichuan, Tibet and Fujian Provinces in China, which is a distinctive species by its pale yellow petaloid basidiomes, simple septate hyphae and small non-amyloid (Zheng *et al.*, 2008). By now, no any chemical investigations have been reported on it. As part of our efforts to discover the structurally diverse and biologically significant metabolites from higher fungi (Liu, 2005, 2006), the investigation of the fruiting bodies of *A. yasuda* has led to the isolation of a new grifolin derivative, named grifolene (1), together with grifolin (2), neogrifolin (3) and grifolic acid (4).

Results and Discussion

Compound 1, obtained as yellow oil, has a molecular formula of $C_{24}H_{32}O_4$ based on HRESI-MS (pos.), showing a quasi-molecular ion at *m z* 385.2369 (calcd. for $C_{24}H_{33}O_4$, 385.2378), requiring nine degrees of unsaturation. The IR spectrum displayed absorption bands of hydroxyl (3445 cm^{-1}) and double bond (1650 cm^{-1}) groups. The ^1H NMR spectrum (Table 1) of 1 in $CDCl_3$ showed signals for three vinyl methyls 1.83 (3H, s), 1.82 (3H, s), 1.58 (3H, s), a phenyl methyl 2.46 (3H, s), four substituted olefinic protons, 6.13 (1H, d, J = 15.5), 5.61 (1H, dt, J

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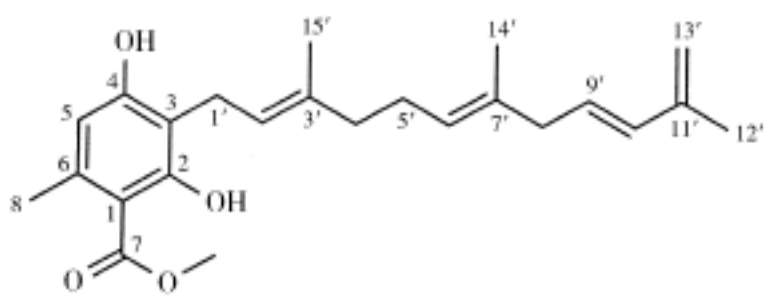
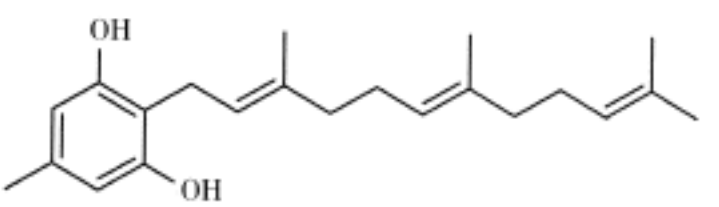
= 15.5, 7.0), 5.27 (1H, t, J = 7.1), 5.11 (1H, t, J = 6.8), and an aromatic proton 6.23 (1H, s). The NMR spectra were similar to those of grifolic acid (4) (Mahiou *et al.*, 1995), and the obvious NMR differences were as follows: the signals at δ 131.0 (s), 124.5 (d), 26.7 (t), 25.7 (q), 17.7 (q) due to the terminal isopentenyl unit in 4 were absent and replaced by newly arising resonances at δ 142.2 (s), 133.9 (d), 128.9 (d), 114.5 (t), 18.7 (q) in 1. In combination with the HMBC correlations (Table 1): from δ_H 1.83 (3H, s, H-12′) to δ_C 133.9 (d, C-10′) and 114.5 (t, C-13′), from δ_H 4.88 (2H, s, H-13′) to δ_C 133.9 (d, C-10′) and 18.7 (q, C-12′), we suggested that there was a 1, 3-pentadiene unit instead of the isopentenyl group. Furthermore, the position of an additional methoxy group can be easily determined at the carboxyl group in aromatic ring by the HMBC correlations (Table 1). Consequently, the structure of 1 was established as shown in Figure 1, named grifolene.

Comparison of the physical and spectroscopic data with the reported data allowed for the identification of compounds 2, 3 and 4, as grifolin (2) (Mahiou *et al.*, 1995), neogrifolin (3) (Nukata *et al.*, 2002) and grifolic acid (4) (Mahiou *et al.*, 1995), respectively.



1



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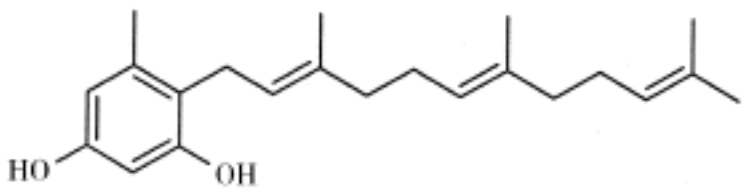

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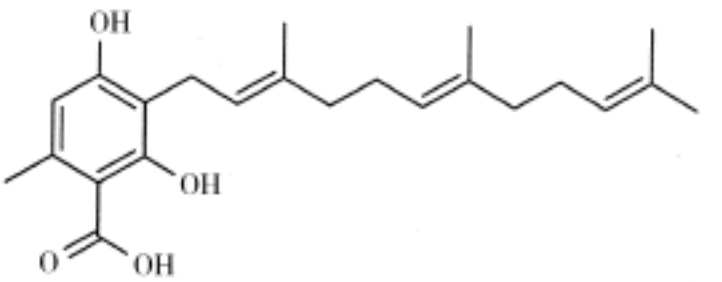

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Fig. 1 Structures of compounds 1-4

Table 1 NMR Spectral Data for Compound 1 in $CDCl_3$

No.	δ_C	δ_H	HMBC	No.	δ_C	δ_H	HMBC
1	111.3 (s)			6′	124.6 (d)	5.11 (1H, t, 6.8)	C-4′, C-7′, C-14′
2	162.6 (s)			7′	134.4 (s)		
3	105.1 (s)			8′	42.9 (t)	2.75 (2H, d, 7.0)	C-6′, C-10′
4	159.4 (s)			9′	128.9 (d)	5.61 (1H, dt, 15.5, 7.0)	C-7′, C-11′
5	111.4 (d)	6.23 (1H, s)	C-1, C-3, C-8	10′	133.9 (d)	6.13 (1H, d, 15.5)	C-8′, C-12′, C-13′
6	140.8 (s)			11′	142.2 (s)		
7	172.7 (s)			12′	18.7 (q)	1.83 (3H, s)	C-10′, C-13′
8	24.2 (q)	2.46 (3H, s)	C-1, C-5	13′	114.5 (t)	4.88 (2H, s)	C-10′, C-12′
1′	22.0 (t)	3.43 (2H, d, 7.1)	C-2, C-4, C-3′	14′	16.2 (q)	1.58 (3H, s)	C-6′, C-8′
2′	121.5 (d)	5.27 (1H, t, 7.1)	C-3, C-4′, C-15′	15′	16.2 (q)	1.82 (3H, s)	C-2′, C-4′
3′	138.9 (s)			-OCH_3	51.8 (q)	3.92 (3H, s)	C-7
4′	39.6 (t)	2.09 (2H, t, 6.3)	C-2′, C-6′	2-OH		12.10 (1H, s)	C-1, C-2, C-3
5′	26.3 (t)	2.13 (2H, dt, 6.8, 6.3)	C-3′, C-7′				

Experimental

General　UV spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. IR spectrum was obtained with a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. NMR spectra were recorded with a Bruker DRX-500 spectrometer in $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.00 ppm) at room temperature. EIMS was taken on a Finnigan-MAT 90 instrument and HRESI-MS recorded with API QSTAR Pulsar i spectrometer. Silica gel (200-300 mesh, Qingdao Marine Chemical Inc., China) and Sephadex LH-20 (Amersham Biosciences, Sweden) were used for column chromatography. Fractions were monitored by TLC and spots were visualized by heating silica gel plates immersed with vanillin-H_2SO_4 in ethanol.

Fungal material　The fresh fruiting bodies of *A. yasuda* were purchased at the wild mushroom market in Nanhua County of Yunnan Province, China, in September 2007 and identified by Prof. Dr. YANG Zhu-Liang. A voucher specimen has been deposited in the Herbarium of Kunming Institute of Botany, CAS.

Extraction and isolation　The fresh fruiting bodies of *A. yasuda* were immersed in ethanol (1∶1, v v) and left at room temperature. The ethanol extract (250 g) was applied on a silica gel column, which eluted stepwise with petroleum ether acetone solvent system. Fraction 1 (2.1 g) from petroleum ether acetone (20∶1, v v) was isolated by silica gel ($CHCl_3$ petroleum ether = 10∶1, v v) to afford 2 (1.9 g). Fraction 2 (1.2 g) from petroleum ether acetone (15∶1, v v) was isolated by silica gel (petroleum ether acetone = 5∶1, v v) to afford 3 (34 mg). Fraction 3 (3.8 g) from petroleum ether acetone (10∶1, v v) was isolated by silica gel (petroleum ether acetone = 10∶1, v v) to afford 4 (2.0 g) and a residue mainly containing 1 (petroleum ether acetone = 5∶1, v v), which was further purified on Sephadex LH-20 ($CHCl_3$ MeOH, 1 1) together with silica gel (petroleum ether $CHCl_3$ = 100∶1, v v) to yield pure compound 1 (3.0 mg) as yellow oil.

Grifolene (1): yellow oil. UV ($CHCl_3$): λ_{max} (log ε) 268 (3.98), 305 (sh, 3.53) nm; IR (KBr) ν 3445, 2931, 1650, 1454, 1441, 1319, 1275, 1196, 1157, 981 cm^{-1}. NMR data and key HMBC correlations: see Table 1. EIMS: *m z* (%) = 384 (1) $[M]^+$, 285 (3), 271 (6), 248 (11), 233 (14), 217 (79), 175 (26), 163 (100), 147 (16). HRESI-MS (pos.): 385.2369 (calcd. for $C_{24}H_{33}O_4$, 385.2378).

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