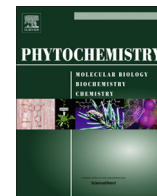




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Chemical constituents from cultures of the basidiomycete *Trichaptum pargamenum*

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ABSTRACT

Four cadinane-type sesquiterpenes and four 13-carbon γ -lactones, together with three known compounds, were isolated from cultures of the basidiomycete *Trichaptum pargamenum*. Their structures were elucidated on the basis of extensive spectroscopic methods. The absolute configurations of two of the cadinane type sesquiterpenes **1** and **3** were confirmed by single crystal X-ray diffractions.

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1. Introduction

The genus *Trichaptum* belongs to order Hymenochaetales. Species of the genus causes a similar fragile, lacy white, pocket rot on both angiosperm and gymnosperm wood. Most species of *Trichaptum* occur in temperate and boreal forests, and 13 species in the genus were found in China (Dai et al., 2009a; Dai 2012). The mushroom *T. pargamenum* (Fr.) G. Cunn. (= *T. bifforme* (Fr.) Ryvarden) has a wide distribution in China (Cui et al., 2008; Dai et al., 2009a), and has been used as a medicinal fungus for treating cancer, fungal, and bacterial diseases in areas of China (Dai et al., 2009b; Yang et al., 2005). The secondary metabolites produced by this fungus have not been reported previously. In the course of ongoing search for novel secondary metabolites, a chemical investigation of cultures of *T. pargamenum*, led to isolation of four new cadinane-type sesquiterpenes (Fig. 1), (+)-(1R,3R,6S,7S,11R)-3,12-dihydroxy- α -muurolene (**1**), (+)-(1R,3R,6S,7S,11S)-3,12-dihydroxy- α -muurolene (**2**), 3 α -hydroxyartemisinic acid (**3**), (+)-(1R,3R,6S,7S,8R,11S)-3,8,12-trihydroxy- α -muurolene (**4**), and four new 13-carbon γ -lactones (Fig. 1), (6Z,11S)-3,4-*trans*-11-oxo-3-methyldodec-*cis*-6-en-4-olide (**5**), (6Z,11S)-3,4-*trans*-11-hydroxy-3-methyldodec-*cis*-6-en-4-olide (**6**), (6Z,11S)-3,4-*trans*-9-hydroxy-3-methyldodec-*cis*-6-en-4-olide (**7**),

(6Z,11S)-3,4-*trans*-9-oxo-3-methyldodec-*cis*-6-en-4-olide (**8**), along with three known compounds, (+)-3 β -hydroxy- α -muurolene (**9**) (Affeld et al., 2009), *ent*-T-muurolol (**10**) (Nagashima et al., 1994), and 2-methyl-6-methylene-oct-7-en-2,3-diol (**11**) (Barrero et al., 1992; Bohlmann et al., 1983). The structures of new compounds were elucidated by means of spectroscopic methods, while the known compounds were identified by comparison with data reported in the literature. According to the medicinal use of this fungus, all isolated compounds were evaluated for their cytotoxicities against five human cancer cell lines.

2. Results and discussion

Compound **1** was obtained as colorless cubic crystals (MeOH). Its molecular formula C₁₅H₂₄O₂ was determined by its HREIMS at *m/z* 236.1782 [M]⁺ (calcd. for 236.1776), corresponding to four degrees of unsaturation. The IR data at 3300 cm⁻¹ corresponded to hydroxy groups. The ¹³C NMR spectroscopic data suggested 15 carbon resonances, which were ascribed to three methyls, three methylenes (including one oxygenated), seven methines (including one oxygenated and two olefinic), and two sp² quaternary carbons, respectively. In the ¹H NMR spectrum (Table 1), signals at δ_{H} 1.80 and 1.69 (each 3H, s) were readily identified as methyl groups connected to double bonds. Meanwhile, the ¹H–¹H COSY spectrum (Fig. 2) had correlations of H-11 with H₂-12 and H₃-13. These data suggested that compound **1** should be a cadinane-type sesquiter-

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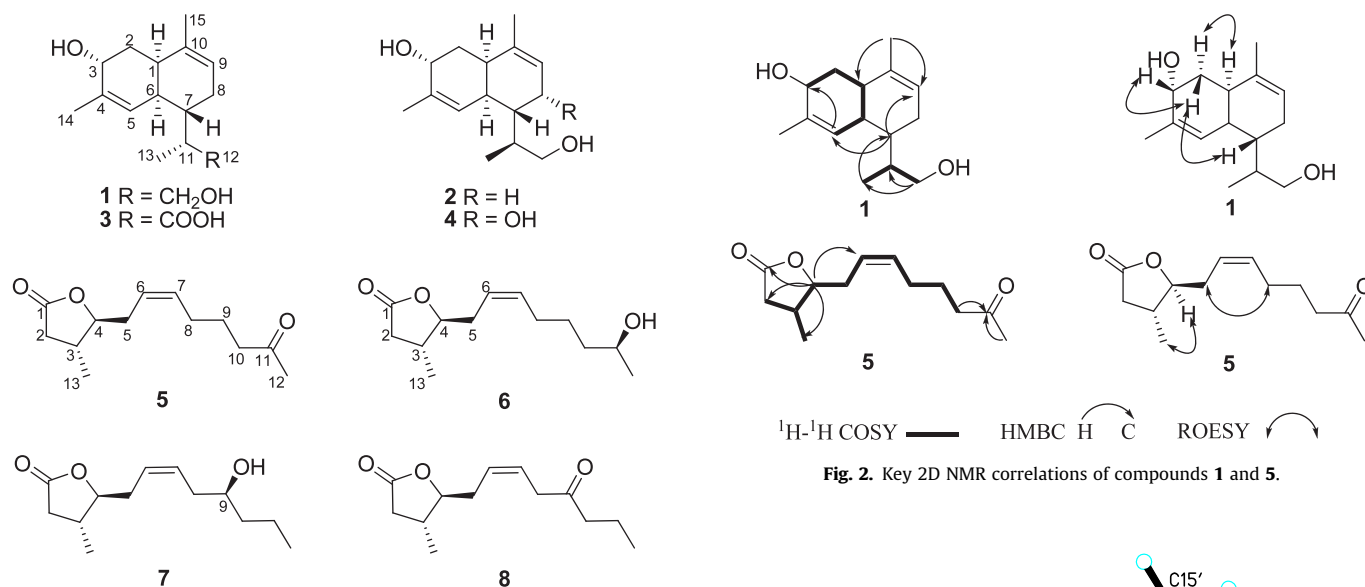
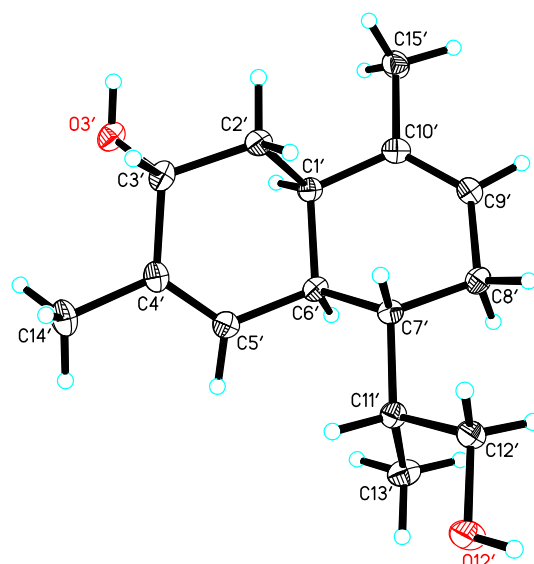


Fig. 1. Structures of compounds 1–8.

ene, with similarities to (+)-3 β -hydroxy- α -muurolene (Affeld et al., 2009). The key difference between them was that the methyl group at C-12 in (+)-3 β -hydroxy- α -muurolene was replaced by a hydroxymethylene (δ_c 66.9, C-12) moiety in compound **1**, as supported by the HMBC correlations (Fig. 2) from δ_H 3.39 (2H, m, H-12) to δ_c 36.0 (d, C-11) and 10.7 (q, C-13). Detailed analysis of the 2D NMR spectroscopic data indicated that the other parts of **1** were the same to those of (+)-3 β -hydroxy- α -muurolene (Affeld et al., 2009). Due to free rotation of bond of C-7/C-11, the stereochemistry of C-11 in **1** could not be established readily. Fortunately, a single crystal X-ray diffraction identified the absolute configuration of **1** as 1*R*,3*R*,6*S*,7*S*,11*R* (Fig. 3). In addition, comparison of the optical rotation data of **1** (+122.2) with those reported in the literature (Affeld et al., 2009; Ohloff and Pawlak, 1970) also supported the absolute structure of **1**. Hence, structure **1** was deduced as (+)-(1*R*,3*R*,6*S*,7*S*,11*R*)-3,12-dihydroxy- α -muurolene.

Compound **2** gave the same molecular formula C₁₅H₂₄O₂ as that of **1** by HREIMS. Comparison of ¹H and ¹³C NMR spectroscopic data of **2** (Tables 1 and 2) with those of **1** suggested that compound **2** exhibited a similar structure to that of **1**. Preliminary analysis of HSQC, ¹H–¹H COSY and HMBC data suggested that compound **2**

Fig. 3. ORTEP drawing of crystal structure of **1**.

had the same overall structure to that of **1**; analysis of the ROESY correlations also suggested that the configurations at C-1, C-3, C-6 and C-7 in **2** were in agreement with those of **1**. However, signif-

Table 1
¹H NMR spectroscopic data for **1**–**4** (δ in ppm; *J* in Hz).

No.	1 ^a	2 ^a	3 ^b	4 ^c
1	2.31, m	2.24, m	2.31, m	2.23, m
2a	1.93, m	1.89, m	1.93, m	1.86, m
2b	1.61, m	1.69, m	1.71, m	1.52, m
3	3.88, t (3.4)	3.95, t (3.4)	3.98, t (3.4)	3.97, t (3.4)
5	5.68, br d (4.2)	5.67, br d (3.3)	5.56, br d (3.1)	5.83, br d (4.2)
6	2.09, m	2.19, m	2.10, m	2.14, m
7	1.79, overlap	1.54, m	2.06, m	2.04, m
8a	1.80, 2H, overlap	1.98, m	1.91, m	4.19, br s
8b		1.79, overlap	1.85, m	
9	5.41, br s	5.40, br s	5.39, br s	5.63, br s
11	1.99, m	1.94, m	2.77, m	2.58, m
12a	3.39, 2H, overlap	3.74, dd (10.5, 4.5)		3.83, t (7.8)
12b		3.46, dd (10.5, 8.6)		3.52, t (7.8)
13	0.86, d (7.0)	0.99, d (6.9)	1.11, d (7.0)	1.14, d (7.2)
14	1.80, s	1.81, s	1.82, s	1.83, s
15	1.69, s	1.68, s	1.70, s	1.79, s

^a Measured at 400 MHz.

^b Measured at 500 MHz.

^c Measured at 600 MHz.

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