Purpuracolide: a New Alliacane Sesquiterpene from the Basidiomycete *Gomphus purpuraceus*

Meng-Yuan Jiang[a, b], Xiao-Long Yang[a, b], Li-Zhen Fang[a, b], Ling Zhang[a, b], Ze-Jun Dong[a], and Ji-Kai Liu[a]

[a] State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100049, China

Reprint requests to Prof. Dr. Ji-Kai Liu. Fax: +86-871-5150227. E-mail: jkliu@mail.kib.ac.cn

Z. Naturforsch. **2008**, *63b,* 1012 – 1014; received April 21, 2008

A new alliacane sesquiterpene named purpuracolide (**1**) was isolated from the fruiting bodies of basidiomycete *Gomphus purpuraceus*. The structure and stereochemistry have been established on the basis of spectroscopic data.

Key words: Alliacane Sesquiterpene, Purpuracolide, *Gomphus purpuraceus*, Basidiomycete

The basidiomycete *Gomphus purpuraceus*, belonging to the Gomphaceae family, is an edible mushroom, distributed in southwest of China [1]. Although the nutrition of *G. purpuraceus* has been reported [2], there are few studies concerning the secondary metabolites produced by this fungus. In our continuing search for biologically active metabolites from basidiomycetes in China [3 – 6], we found that the fruiting bodies of *G. purpuraceus* collected at Nanhua of Yunnan province produced an alliacane sesquiterpene (**1**). In 1977, Hanson and Thaller isolated a novel sesquiterpene, alliacolide from cultures of the basidiomycete *Marasmius alliaceus* [7]. Full spectroscopic analysis, as well as X-ray crystallography, revealed a compact arrangement of an epoxide and a unique tertiary β-hydroxy γ-lactone. An exhaustive study of the crude extracts provided several other metabolites, including the biologically active constituents alliacol A and B. These substrates demonstrate effective inhibition of DNA synthesis in ascetic Ehrlich carcinoma [8]. This report deals with the isolation and structure elucidation of **1**.

Experimental Section

General experimental procedures

Optical rotation was measured on a Horiba SEPA-300 polarimeter. The IR spectrum was obtained on a Bruker Tensor 27 instrument with KBr pellets. NMR spectra were recorded on Bruker AV-400 and DRX-500 spectrometers in $CDCl_3$ with TMS as internal standard. The EI-MS was recorded with a VG Autospec-3000 spectrometer. The HRESI-MS was recorded with an API QSTAR Pulsar 1 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 sprayed with 10 % H_2SO_4 in ethanol.

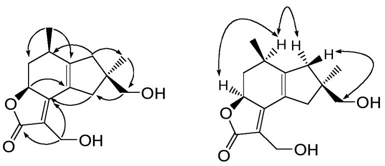

Fig. 1. Key HMBC and ROESY correlations of compound **1**.

Fungal material

The basidiomycete *G. purpuraceus* was collected at Nanhua of Yunnan province, China, in September 2007 and identified by Prof. Mu Zang, Kunming Institute of Botany, Chinese Academy of Sciences (CAS).

Extraction and isolation

Fresh fruiting bodies (3.0 kg) were extracted three times with acetone / 95 % EtOH (3 : 1) at r. t. After removal of the solvent by evaporation, the residue (34.0 g) was suspended in H_2O and then successively extracted three times with ethyl acetate. After evaporation, the organic layer gave 20.0 g of an oily residue which was chromatographed on a

Table 1. ^{13}C and ^{1}H NMR (100 and 400 MHz, in $CDCl_3$, δ in ppm, J in Hz) data for **1**.

Position	δ_C	δ_H
1	31.9, d	2.60, m
2	38.0, t	2.52, ddd, J = 11.7, 5.3, 4.7 1.40, ddd, J = 12.9, 11.7, 11.3
3	79.2, d	4.89, dd, J = 12.9, 4.7
4	157.6, s	
5	126.9, s	
6	43.9, t	2.63, d, J = 18.8 2.09, d, J = 18.8
7	43.4, s	
8	41.7, t	2.86, d, J = 15.5 2.32, d, J = 15.5
9	156.6, s	
10	19.3, q	1.15, d, J = 6.7
11	117.8, s	
12	175.0, s	
13	54.8, t	4.44, d, J = 13.5 4.39, d, J = 13.5
14	70.3, t	3.52, s
15	25.1, q	1.11, s

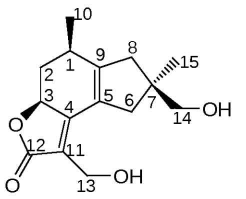

Fig. 2. The structure of compound **1**.

silica gel column and eluted stepwise with $CHCl_3$/MeOH (100 : 0, 40 : 1, 20 : 1, 10 : 1, 5 : 1, 1 : 1) to afford six fractions (A – F). Compound **1** (3.8 mg) was obtained from fraction B by repeated Sephadex LH-20 ($CHCl_3$/MeOH, 1 : 1) and prep. TLC ($CHCl_3$/MeOH 12 : 1).

Identification

Purpuracolide (**1**), colorless oil. $C_{15}H_{20}O_4$. – $[\alpha]_D^{20}$ = −43.8° (c = 0.18, $CHCl_3$). – UV/Vis ($CHCl_3$): λ_{max} (lgε_{max}) = 284 nm (4.11). – IR (KBr): ν = 3429, 2958, 2927, 2873, 1744, 1651, 1459, 1378, 1040 cm^{-1}. – ^{1}H and ^{13}C NMR (400 MHz, $CDCl_3$): see Table 1. – MS (EI, 70 eV): m/z (%) = 264 (2) $[M]^+$, 246 (12), 215 (100), 201 (5). – HRMS((+)-ESI): m/z = 287.1249 (calcd. 287.1259 for $C_{15}H_{20}O_4Na$, $[M + Na]^+$).

Result and Discussion

Compound **1** was obtained as a colorless oil. The molecular formula of **1** was determined to be $C_{15}H_{20}O_4$ on the basis of HRESI-MS (calcd. for $C_{15}H_{20}O_4Na$, m/z = 287.1259; found 287.1249). The IR spectrum of **1** revealed the presence of hydroxyl (3429 cm^{-1}) and carbonyl (1744 cm^{-1}) groups. The ^{13}C NMR spectrum (Table 1) exhibited 15 carbon signals including one ester carbonyl (δ = 175.0), four olefinic quaternary carbons (δ = 157.6, 156.6, 126.9, 117.8), five methylenes (δ = 70.3, 54.8, 43.9, 41.7, 38.0), two methines (δ = 79.2, 31.9), one quaternary carbon (δ = 43.4) as well as two methyl (δ = 25.1, 19.3) carbons. Correspondingly, the ^{1}H NMR spectrum revealed one oxymethine (δ = 4.89, dd, J = 12.9, 4.7 Hz), two oxymethylenes (δ = 4.44, 1H, d, J = 13.5 Hz; 4.39, 1H, d, J = 13.5 Hz and δ = 3.52, 2H, s), three methylenes (δ = 1.40 – 2.86), one methine (δ = 2.60, m), and two methyl groups (δ = 1.15, d, J = 6.7 Hz; δ = 1.11, s).

Interpretation of HMBC data showed the following key ^{3}J correlations: H-10 to C-2 and C-9; H-3 to C-1 and C-5; H-8 to C-1, C-5, C-6, C-14, and C-15; H-6 to C-4, C-8, C-9 and C-15; H-15 to C-6, C-8 and C-14 (Fig. 1). The correlating peaks indicated that **1** possessed a carbon skeleton of an alliacane sesquiterpene [7].

The relative configuration of **1** was established by a ROESY experiment. Considering that Me-10 of all alliacanoids possesses the β-orientation [7 – 11], Me-10 of **1** was also presumed to be β-oriented. NOE correlations were observed between H-1 and H-3, suggesting that both protons possessed α-orientations. This configuration of H-3 was also supported by the coupling constants value (Table 1). Observed NOE correlations between H-1 and H-8α, and between H-8β and H-14 indicated that C-14 was β-oriented. On the basis of the evidences summarized above, the structure of purpuracolide (**1**) was deduced to be that shown in Fig. 2.

Acknowledgement

This project was supported by the Chinese Academy of Sciences (KSCX1-YW-R- 24; KSCX2-YW-G-025).

[1] X. L. Mao, *The Macrofungi in China*, Henan Science and Technology Press, Zhengzhou, **2000**, pp. 388.

[2] a) A. H. Tan, S. G. Zhang, F. Z. Liu, *Acta Edulis Fungi* **2001**, *4*, 15 – 18; b) A. H. Tan, F. Z. Liu, *Journal of Yangtze University (Nat. Sci. Edit., Agri. Sci. V.)* **2006**, *3*, 172 – 173; c) A. H. Tan, F. Z. Liu, S. G. Zhang, *Acta Edulis Fungi* **2003**, *4*, 24 – 28.

[3] J. K. Liu, *Chem. Rev.* **2006**, *106*, 2209 – 2223.

[4] J. K. Liu, *Chem. Rev*. **2005**, *105*, 2723 – 2744.
[5] J. K. Liu, *Heterocycles* **2002**, *57*, 157 – 167.
[6] D. Z. Liu, F. Wang, T. G. Liao, J. G. Tang, W. Steglich, H. J. Zhu, J. K. Liu, *Org. Lett*. **2006**, *25*, 5749 – 5752.
[7] T. J. King, I. W. Farrell, T. G. Halsall, V. Thaller, *J. Chem. Soc., Chem. Comm*. **1977**, 727 – 728.
[8] T. Anke, W. H. Watson, B. M. Giannetti, W. Steglich, *J. Antibiot*. **1981**, *34*, 1271 – 1277.
[9] L. W. Farrell, T. G. Halsall, V. Thaller, A. P. W. Bradshaw, J. R. Hanson, *J. Chem. Soc., Perkin Trans*. **1981**, 1790 – 1793.
[10] A. P. W. Bradshaw, J. R. Hanson, D. N. Kirk, P. M. Scopes, *J. Chem. Soc., Perkin Trans*. **1981**, 1794 – 1795.
[11] A. G. Avent, J. R. Hanson, P. B. Hitchcock, B. L. Yeoh, *J. Chem. Soc., Perkin Trans*. **1985**, 2749 – 2751.