

Short Communication

New phenyl-ethanediols from the culture broth of *Boletus edulis*

Wan-Qiu Yang^{1,2}, Xiang-Dong Qin^{1,2}, Hong-Jun Shao^{1,2}, Li-Zhen Fang^{1,2}, Fei Wang^{1,2}, Zhi-Hui Ding¹, Ze-Jun Dong¹ and Ji-Kai Liu¹

¹ State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, P.R. China

² Graduate School of Chinese Academy of Sciences, Beijing, P.R. China

A new phenyl-ethanediol, (1*S*)-(4-acetylphenyl)-1, 2-ethanediol (1), and a new natural product, (1*S*)-(3-ethenylphenyl)-1, 2-ethanediol (2), were isolated from the culture broth of the basidiomycete *Boletus edulis* together with three related known compounds, 1-(4-ethylphenyl)-1, 2-ethanediol (3), 1-(3-ethylphenyl)-1, 2-ethanediol (4) and 1-(3-formylphenyl)-ethanone (5). Their structures were elucidated by spectroscopic methods including extensive 2D-NMR techniques.

Keywords: Phenyl-ethanediol / Isolation / Basidiomycete / *Boletus edulis* / 2D-NMR

Received: August 25, 2006; returned for modification: August 29, 2006; accepted: October 17, 2006

DOI 10.1002/jobm.200610260

Introduction

Yunnan Province, southwest of China, is one of the areas with the richest and diverse bio-resources in the world. Fungi in these bio-resources belong to the most productive biological sources producing a diverse variety of secondary metabolites. There are some reports on chemical constituents for *Boletus edulis*, most of them are focus on fatty acids and nutrition value (Yilmaz *et al.* 2006, Wang *et al.* 2003). Recently, Steglich has isolated a series of calopins from *Boletus calopus* (Hellwig *et al.* 2002), and boletocrocins from *B. laetissimus* and *B. rufo-aureus* (Kahner *et al.* 1998). As one part of our work on the biologically active natural products from higher fungi of Yunnan Province, China (Liu 2005, Wang 2004, Qin 2006), the chemical constituents from the culture broth of *B. edulis* were investigated. A new phenyl-ethanediol, (1*S*)-(4-acetylphenyl)-1, 2-ethanediol (1) (Fig. 1), and a new natural product, (1*S*)-(3-ethenylphenyl)-1, 2-ethanediol (2), were isolated from the culture broth of the basidiomycete *Boletus edulis* together with three related known compounds, 1-(4-ethylphenyl)-1, 2-ethanediol (3), 1-(3-ethylphenyl)-1, 2-ethanediol (4) and 1-(3-formylphenyl)-ethanone (5) (Nurettin 1993,

Rodney *et al.* 2005). We describe herein the isolation and structural elucidation of (1*S*)-(4-acetylphenyl)-1, 2-ethanediol (1).

Materials and methods

Column chromatography (CC)

Optical rotations were measured on a Horiba SEPA-300 polarimeter. IR spectra were obtained with a Tensor 27 with KBr pellets. UV spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. NMR spectra were recorded on a Bruker DRX-500 spectrometer. EI-MS were recorded with a VG Autospec-3000 spectrometer. ESI-MS and HR-ESI-MS were recorded with an API QSTAR Pulsar 1 spectrometer. HPLC was measured on Agilent 1100 series using XTerra Prep RP-18 column.

Fungal material and fermentation

The fresh fruiting bodies of *B. edulis* were collected at Ailao Mountain, Yunnan Province, P. R. China, in August 2005. A voucher specimen was deposited at the herbarium of Kunming Institute of Botany, Chinese Academy of Sciences. The mycelial cultures were derived from tissue plugs. The culture medium consisted of potato (peel off) 200 g, glucose 20 g, KH₂PO₄ 3 g, MgSO₄ 1.5 g, citric acid 0.1 g and thiamin hydrochloride 10 mg in 1 l of sterilized water. Reagent bottles were

Correspondence: Prof. Dr. Ji-Kai Liu, State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, P.R. China.
Fax: +86-871-5150227
E-mail: jkliu@mail.kib.ac.cn

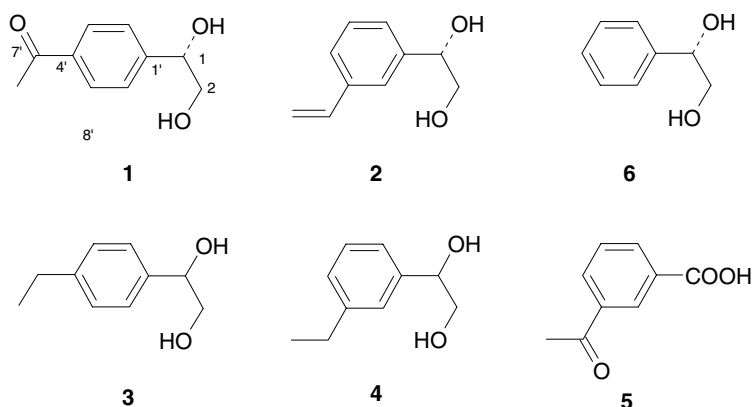


Figure 1. Structures of compounds 1–6.

used as flask (size: 500 ml; volume of media: 300 ml). The pH was adjusted to 6.5 before autoclaving. Fermentation was carried out on a shaker at 22 °C and 140 rpm for 16 days.

Extraction and isolation

The culture broth (10 l) was filtered and passed through a D101-resin column eluting with H₂O and 95% EtOH. The 95% EtOH eluent was evaporated to give a brown residue, and was then extracted by AcOEt to afford a residue (1.3 g), which was subjected to CC (silica gel column, 2.5 × 25 cm, CHCl₃/MeOH). Fr. A eluted with CHCl₃/MeOH (19/1, v/v) was further isolated by Sephadex LH-20 (1.3 × 100 cm) using CHCl₃/MeOH (1/1, v/v) to give 60 mg of a mixture of compounds 2–5. This mixture was purified by preparative HPLC (isolation conditions: a. column: RP-18; 2.12 × 25 cm; a. mobile phase: 35% MeOH/H₂O; b. flow rate: 10 ml/min) to afford compound 5 (4 mg, *t_R* = 49 min), compound 2 (3 mg, *t_R* = 60 min) and a mixture of compounds 3 and 4 (12 mg, *t_R* = 80 min). Fr. B eluted with CHCl₃/MeOH (10/1, v/v) was purified by Sephadex LH-20 (1.3 × 100 cm) using CHCl₃/MeOH (1/1, v/v) to give crude 1 (26 mg), which was further purified by preparative HPLC (isolation conditions: a. column: RP-18; 2.12 × 25 cm; a. mobile phase: 11% MeOH/H₂O; b. flow rate: 10 ml/min) to afford compound 1 (2 mg, *t_R* = 56 min).

Results and discussion

Compound 1 was obtained as oil. Its molecular formula was determined to be C₁₀H₁₂O₃ by EI-MS ($[M]^+$ = 180) and ¹³C-NMR (DEPT: 1 × Me, 1 × CH₂, 5 × CH, 3 × C), which was also confirmed by HR-ESI-MS ($[M + Na]^+$ 203.0687, calcd. 203.0684). Total ten signals in the ¹³C-NMR spectrum suggested the existence of a phenyl group (2 × CH

at δ = 127.7, 2 × CH at δ = 129.5, C at δ = 137.7, C at δ = 149.3), a C=O (δ = 200.7), a CH–O (δ = 75.4), a CH₂–O (δ = 68.5) and a CH₃ (δ = 26.7). In the ¹H-NMR spectrum, the signals at δ = 7.51 (d, *J* = 8.3) and 7.97 (d, *J* = 8.3) suggested a 1, 4-disubstituted aromatic ring system; a methyl signal at δ = 2.59 (s) indicated the presence of a –COCH₃ group. In the ¹H, ¹H-COSY spectrum, the apparent correlation peaks between δ = 4.75 (dd, *J* = 6.8, 4.8) and 3.60 (dd, *J* = 11.3, 6.8), 3.64 (dd, *J* = 11.3, 4.8) were observed, indicating a –O–CH–CH₂–O– linking. Considering the molecular formula C₁₀H₁₂O₃ and its HMBC spectrum (Fig. 2), 1 was therefore elucidated as 1-(4-acetylphenyl)-1, 2-ethanediol. Because the optical rotations of 1 ($[\alpha]_D^{17.6}$ = 9.1, *c* = 0.39, MeOH) and 6 ($[\alpha]_D^{17.6}$ = 29.3, *c* = 1, EtOH) (Bosetti *et al.* 1992) are similar, the absolute configuration of 1 at C-1 was decided to be S.

Compound 2 was also obtained as oil. Its molecular formula was determined to be C₁₀H₁₂O₂ by EI-MS ($[M]^+$ = 164) and ¹³C-NMR (DEPT: 2 × CH₂, 6 × CH, 2 × C), which was also confirmed by HR-ESI-MS ($[M + Na]^+$ 187.0736, calcd. 187.0734). Ten signals in the ¹³C-NMR spectrum were probably due to the existence of a phenyl group and a C=C group (δ = 114.1, 125.2, 126.4, 127.0, 129.5, 138.2, 139.0, 143.7), a CH–O group (δ = 75.9) and a CH₂–O group (δ = 68.7). Analyzing the ¹H-NMR spectrum for 2, a set of signals at δ = 7.44 (s), 7.33 (d, *J* = 7.2), 7.29 (dd, *J* = 7.4, 7.2) and 7.25 (d, *J* = 7.4) indicated the existence of a 1, 3-disubstituted aromatic ring

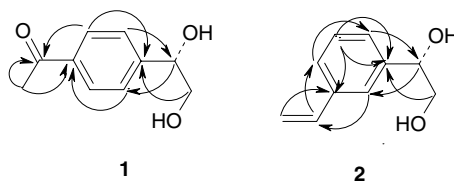


Figure 2. Selected HMBC correlations of compounds 1–2.

Table 1. ^1H - and ^{13}C -NMR Data (CD_3OD) for **1** and **2**.

Position	1		2	
	δ (C)	δ (H)	δ (C)	δ (H)
C(1)	75.4 (CH)	4.75 (dd, $J = 6.8, 4.8$)	75.9 (CH)	4.67 (dd, $J = 7.0, 4.9$)
C(2)	68.5 (CH_2)	3.60 (dd, $J = 11.3, 6.8$) 3.64 (dd, $J = 11.3, 4.8$)	68.7 (CH_2)	3.59 (dd, $J = 11.3, 7.0$) 3.63 (dd, $J = 11.3, 4.9$)
C(1')	149.3 (C)		143.7 (C)	
C(2')	127.7 (CH)	7.51 (d, $J = 8.3$)	125.2 (CH)	7.44 (s)
C(3')	129.5 (CH)	7.97 (d, $J = 8.3$)	139.0 (C)	
C(4')	137.7 (C)		126.4 (CH)	7.33 (d, $J = 7.2$)
C(5')	129.5 (CH)	7.97 (d, $J = 8.3$)	129.5 (CH)	7.29 (dd, $J = 7.4, 7.2$)
C(6')	127.7 (CH)	7.51 (d, $J = 8.3$)	127.0 (CH)	7.25 (d, $J = 7.4$)
C(7')	200.7 (C)		138.2 (CH)	6.73 (dd, $J = 17.6, 11.0$)
C(8')	26.7 (CH_3)	2.59 (s)	114.1 (CH_2)	5.21 (d, $J = 11.0$) 5.77 (d, $J = 17.6$)

system; $\delta = 5.21$ (d, $J = 11.0$), 5.77 (d, $J = 17.6$), 6.73 (dd, $J = 17.6, 11.0$) were apparently due to a $-\text{CH}=\text{CH}_2$ group. In its ^1H , ^1H -COSY spectrum, the obvious correlation signals between $\delta = 4.67$ (dd, $J = 7.0, 4.9$) and 3.59 (dd, $J = 11.3, 7.0$), 3.63 (dd, $J = 11.3, 4.9$) were observed, indicating a $-\text{O}-\text{CH}-\text{CH}_2-\text{O}-$ linking. Considering the molecular formula of $\text{C}_{10}\text{H}_{12}\text{O}_2$ and its HMBC spectrum (Fig. 2), compound **2** was elucidated as 1-(3-ethenylphenyl)-1, 2-ethanediol. According to the optical rotations, the configuration of compound **2** ($[\alpha]_{\text{D}}^{16.8} = 8.7$, $c = 0.50$, MeOH) at C-1 was also decided to be S.

Comparison of the physicochemical properties with reported data allowed to identify three related known components as 1-(4-ethylphenyl)-1, 2-ethanediol (**3**), 1-(3-ethylphenyl)-1, 2-ethanediol (**4**) and 1-(3-formylphenyl)-ethanone (**5**) (Nurettin 1993).

(1S)-(4-acetylphenyl)-1,2-ethanediol (**1**) Oil. $[\alpha]_{\text{D}}^{17.6} = 9.1$ ($c = 0.39$, MeOH). IR (KBr): $\nu = 3417, 2925, 2854, 1679, 1609, 1573, 1411, 1385, 1362, 1273, 1082 \text{ cm}^{-1}$. UV (MeOH): 252 nm . ^1H - and ^{13}C -NMR: see Table 1. MS (EI, 70eV): m/z (%) = 180 (**3**) [M^+], 165 (9), 149 (100), 134 (13), 120 (8), 106 (28), 91 (14), 77 (34). HR-ESI-MS (pos.): ($[\text{M}^+ + \text{Na}]$ 203.0687 , calc. 203.0684).

(1S)-(3-ethenylphenyl)-1,2-ethanediol (**2**): Oil. $[\alpha]_{\text{D}}^{16.8} = 8.7$ ($c = 0.50$, MeOH). IR (KBr): $\nu = 3321, 3086, 3064, 2933, 2868, 1630, 1602, 1581, 1403, 1088, 994 \text{ cm}^{-1}$. UV (MeOH): 249 nm . ^1H - and ^{13}C -NMR: Table 1. EI-MS: m/z (%) = 164 (29) [M^+], 133 (100), 115 (8), 105 (86), 77 (35). HR-ESI-MS (pos.): ($[\text{M}^+ + \text{Na}]$ 187.0736 , calc. 187.0734).

References

- Hellwig, V., Dasenbrock, J., Gräf, C., Kahner, L., Schumann, S. and Steglich, W., 2002. Calopins and cyclocalopins – bitter principles from *Boletus calopus* and related mushrooms. Eur. J. Org. Chem., 2895–2904.
- Kahner, L., Dasenbrock, J., Spiteller, P., Steglich, W., Marumoto, R. and Spiteller, M., 1998. Polyene pigments from fruitbodies of *Boletus laetissimus* and *B. rufo-aureus* (basidiomycetes). Phytochemistry, **49**, 1693–1697.
- Yilmaz, N., Solmaz, M., Türkekul, İ. and Elmastaş, M., 2006. Fatty acid composition in some wild edible mushrooms growing in the middle Black Sea region of Turkey. Food Chem., **99**, 168–174.
- Wang, M.S. and Lian, B., 2003. studying on *Boletus edulis*. Guizhou Forestry Sci. Tech., **31**, 34–38.
- Liu, J.K., 2005. N-Containing Compounds of Macromycetes. Chem. Rev., **105**, 2723–2744.
- Ma, B.J. and Liu, J.K., 2005. A new bitter diterpenoid from *Sarcodon scabrosus*. J. Basic Microbiol., **45**, 328–330.
- Qin, X.D., Dong, Z.J., Liu, J.K., Yang, L.M., Wang, R.R., Zheng, Y.T., Lu, Y., Wu, Y.S. and Zheng, Q.T., 2006. Concentricolide, an anti-HIV agent from the ascomycete *Daldinia concentrica*. Helv. Chim. Acta, **89**, 127–133.
- Rodney, B. and Peter, H., 2005. Rubber compositions useful as cushion gum in retreading procedures for tires. WO 2005108408, 50pp.
- Nurettin, Y., 1993. Isolation and characterization of dibenzoated aromatic compounds. Turk. J. Chem., **17**, 208–214.
- Bosetti, A., Bianchi, D., Cesti, P., Golini, P. and Spezia, S., 1992. Enzymatic resolution 1,2-diol: comparison between hydrolysis and transesterification reactions. J. Chem. Soc. Perkin Trans. I, 2395–2398.