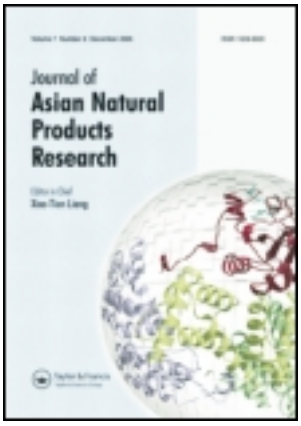

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Three new phenyl-ethanediols from the fruiting bodies of the mushroom *Fomes fomentarius*

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Three new phenyl-ethanediols, (1*R*)-(3-ethenylphenyl)-1,2-ethanediol (**1**), (1*R*)-(3-formylphenyl)-1,2-ethanediol (**2**), and (1*R*)-(3-acetophenyl)-1,2-ethanediol (**3**), were isolated from the fruiting bodies of the mushroom *Fomes fomentarius*, together with two related known compounds, (3-ethylphenyl)-1,2-ethanediol (**4**) and (4-acetophenyl)-1,2-ethanediol (**5**). Their structures were elucidated by spectroscopic methods including extensive 2D NMR techniques. Compounds **1**–**3** showed weak antimicrobial activity.

Keywords: *Fomes fomentarius*; ethanediol; antimicrobial activity

1. Introduction

Mushroom *Fomes fomentarius* is widely distributed in large areas of China [1]. Its fruiting bodies were used traditionally as a folk medicine for the treatment of esophageal, gastric, and uterine cancers [2]. Modern pharmacological researches have identified that the crude extract of *F. fomentarius* had multi-bioactivities, such as antitumor, antioxidant, enhancement of immune function, etc. [3–5]. Previous investigations on the chemical constituents of *F. fomentarius* have revealed a number of steroids [6]. This paper describes the isolation and structural elucidation of three new phenyl-ethanediol compounds, (1*R*)-(3-ethenylphenyl)-1,2-ethanediol (**1**), (1*R*)-(3-formylphenyl)-1,2-ethanediol (**2**), and (1*R*)-(3-acetophenyl)-1,2-ethanediol (**3**), together with two known compounds, (3-ethylphenyl)-1,2-ethanediol (**4**) and (4-acetophenyl)-1,2-ethanediol (**5**) (Figure 1). Their structures have been elucidated on the basis of spectroscopic analysis, especially 2D NMR experiments.

2. Results and discussion

Compound **1** was obtained as a colorless oil. Its molecular formula was determined to be $C_{10}H_{12}O_2$ by HR-ESI-MS data at *m/z* 187.0732 $[M + Na]^+$ in combination with ^1H and ^{13}C NMR data (Table 1). The IR spectrum showed the presence of hydroxy groups (3407 cm^{-1}). Ten signals in the ^{13}C NMR spectrum were probably due to the existence of a phenyl group and a C═C group (δ_C 114.3, 123.9, 125.5, 125.9, 128.7, 136.5, 137.8, and 140.7), a CH—O group (δ_C 74.6) and a CH_2—O group (δ_C 68.0). In the ^1H NMR spectrum, proton signals at δ_H 7.41 (1H, s, H-2), 7.36 (1H, d, $J = 7.6$ Hz, H-4), 7.32 (1H, dd, $J = 7.6$, 7.4 Hz, H-5), and 7.25 (1H, d, $J = 7.4$ Hz, H-6) indicated the existence of a 1,3-disubstituted aromatic ring system, whereas the signals at δ_H 5.28 (1H, d,

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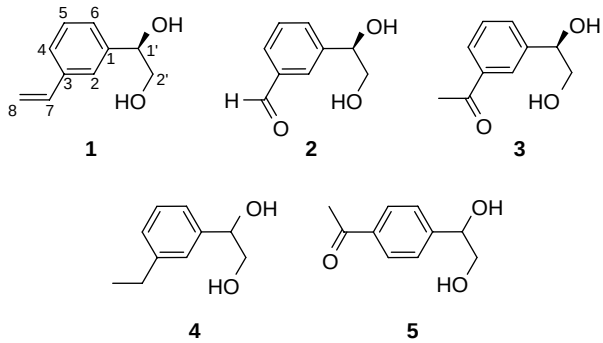

Figure 1. Structures of compounds **1**–**5**.

$J = 11.0$ Hz), 5.77 (1H, d, $J = 17.6$ Hz), and 6.73 (1H, dd, $J = 17.6$, 11.0 Hz) revealed a —CH═CH_2 group. These data indicated that the structure of **1** was similar to that of (1*S*)-phenylethane-1,2-diol [7]. However, the optical rotations of **1** ($[\alpha]_D^{18.2}$ -27.7) suggested the absolute configuration of C-1′ in **1** be *R*, by comparison with that of (1*S*)-phenylethane-1,2-diol ($[\alpha]_D^{18.2}$ $+29.3$) [8]. Therefore, compound **1** was elucidated as (1*R*)-(3-ethenylphenyl)-1,2-ethanediol.

Compound **2**, a colorless oil, possessed a molecular formula $C_9H_{10}O_3$ as established by the HR-ESI-MS at *m/z* 167.0707 $[M + H]^+$. The IR spectrum showed the presence of carbonyl (1696 cm^{-1}) and hydroxy (3410 cm^{-1}) groups. The ^1H and ^{13}C NMR data (Table 1) were very similar to those of **1** except for a CHO group at δ_C 194.4 (d, C-7) in **2** instead of a C═C group in **1**. The carbon was assigned to C-7 as supported by HMBC (Figure 2) correlations from H-2 at δ_H 7.95 (1H, s) and H-4 at δ_H 7.82 (1H, d, $J = 7.5$ Hz) to C-7 at δ_C 194.4 (d). Other 2D NMR data (HSQC and HMBC) suggested that other parts were the same as those of **1**. According to the negative optical rotation of **2** ($[\alpha]_D^{21.9}$ -2.1), the absolute configuration at C-1′ was also decided to be *R*. Thus, compound **2** was elucidated as (1*R*)-(3-formylphenyl)-1,2-ethanediol.

Compound **3** was obtained as a colorless oil. Its molecular formula was established as $C_{10}H_{12}O_3$ by the positive HR-ESI-MS at *m/z* 203.0685 $[M + Na]^+$. The IR spectrum showed absorption bands at 3416 and 1683 cm^{-1}, corresponding to the hydroxy and carbonyl groups, respectively. The ^1H and ^{13}C NMR data (Table 1) were very similar to those of **2** except for signals at δ_H 2.62 (3H, s) and δ_C 27.0 (q, C-8), showing a methyl connected to the carbonyl group, as confirmed by HMBC correlations from H-2 at δ_H 8.03 (1H, s) and H-4 at δ_H 7.91 (1H, d, $J = 7.5$ Hz) to C-7 at δ_C 200.7 (s), and from H-8 at δ_H 2.62 (3H, s) to C-2 at δ_C 127.6 (d) and C-3 at δ_C 138.5 (s). Detailed analysis of HSQC and HMBC spectra (Figure 2) indicated that other parts were same as those of **2**. According to the negative optical rotation of **3** ($[\alpha]_D^{22.2}$ -5.5), the absolute configuration at C-1′ was also decided to be *R*. Compound **3** was, therefore, elucidated as (1*R*)-(3-acetophenyl)-1,2-ethanediol.

The known compounds were identified as (3-ethylphenyl)-1,2-ethanediol (**4**) [9] and (4-acetophenyl)-1,2-ethanediol (**5**) [7] by comparison of their spectroscopic data with those reported in the literatures.

Compounds **1**, **2**, and **3** were tested for antimicrobial activity (positive control: rifampicin) by the disk-diffusion method [10]. The diameters of the inhibition zones are presented in Table 2. The result indicated that three compounds from *F. fomentarius* had weak inhibitory activity on *Bacillus subtilis* ATCC 6633

Table 1. ^{1}H and ^{13}C NMR spectroscopic data of compounds **1**–**3** (J in Hz).

	1[a]		**2**[b]		**3**[b]	
No.	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1′	74.6 d	4.84 (1H, dd, 8.3, 3.5)	75.3 d	4.72 (1H, dd, 5.0, 6.8)	75.5 d	4.76 (1H, dd, 5.0, 6.8)
2′	68.0 t	3.68 (1H, dd, 11.3, 8.3)	68.6 t	3.59 (1H, dd, 11.3, 5.0)	68.7 t	3.65 (1H, dd, 11.3, 5.0)
		3.78 (1H, dd, 11.3, 3.5)		3.58 (1H, dd, 11.3, 6.8)		3.63 (1H, dd, 11.3, 6.8)
1	140.7 s		145.1 s		144.5 s	
2	123.9 d	7.41 (1H, s)	128.8 d	7.95 (1H, s)	127.6 d	8.03 (1H, s)
3	137.8 s		138.2 s		138.5 s	
4	125.5 d	7.36 (1H, d, 7.6)	130.0 d	7.82 (1H, d, 7.5)	128.8 d	7.91 (1H, d, 7.5)
5	128.7 d	7.32 (1H, dd, 7.4, 7.6)	130.2 d	7.56 (1H, dd, 7.5, 7.5)	129.8 d	7.49 (1H, dd, 7.5, 7.5)
6	125.9 d	7.25 (1H, d, 7.4)	134.0 d	7.71 (1H, d, 7.5)	132.7 d	7.64 (1H, d, 7.5)
7	136.5 d	6.73 (1H, dd, 17.6, 11.0)	194.4 d	10.0 (1H, s)	200.7 s	
8	114.3 t	5.28 (1H, d, 11.0)			27.0 q	2.62 (3H, s)
		5.77 (1H, d, 17.6)				

[a] 400 and 100 MHz, in $CDCl_3$.
[b] 600 and 150 MHz, in methanol-d_4.

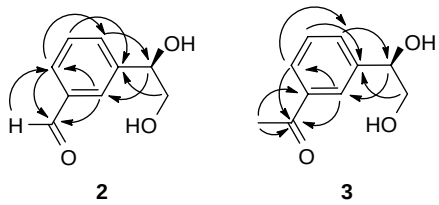

Figure 2. Key HMBC correlations of compounds **2** and **3**.

and *Pseudomonas aenlgimosa* ATCC 9027 (Table 2).

3. Experimental

3.1 General experimental procedures

Optical rotations were measured with a Horiba SEPA-300 polarimeter. UV spectra were obtained using a Shimadzu UV-2401A spectrophotometer. A Tenor 27 spectrophotometer was used for scanning IR spectroscopy using KBr pellets (Bruker Optics GmbH, Ettlingen, Germany). NMR spectra were run on Avance III 600, Bruker DRX-500, and Bruker AM-400 spectrometers with tetramethylsilane as an internal standard (Bruker BioSpin GmbH, Rheinstetten, Germany). Chemical shifts (δ) were expressed in ppm with reference to the solvent signals. HR-ESI-MS were obtained on an API-Qstar-Pulsar-1 spectrometer (MDS Sciex, Concord, Ontario, Canada). Column chromatography was carried out on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co. Ltd, Qingdao, China), Sephadex LH-20 (Pharmacia, Piscataway, NJ, USA), and RP-18 (20–45 μm, Fuji Silysia Chemical Ltd, Kasugai, Aichi, Japan). An Agilent 1100 series instrument equipped with Agilent ZORBAX SB-C18 column (5 μm, 4.6 mm × 150 mm) was used for the HPLC analysis, and a semi-preparative Agilent ZORBAX SB-C18 column (5 μm, 9.4 mm × 150 mm) was used for the sample preparation (Agilent, Santa Clara, USA). Fractions were monitored by thin layer chromatography (GF 254, Qingdao Haiyang Chemical Co. Ltd), and spots were visualized by 10% H_2SO_4 in ethanol.

Table 2. Antibacterial activities of compounds **1**–**3**.

Compound	Diameter of the inhibition zone (mm)	
	B. subtilis (ATCC 6633)	*P. aenlgimosa* (ATCC 9027)
1	8.0	9.0
2	10.0	10.0
3	9.0	10.0
Rifampicin[a]	31.0	28.0

[a] Positive control.

3.2 Fungus material

The fruiting bodies of *F. fomentarius* were collected from Heilongjiang Province, China, in September 2010. A voucher specimen (12-34124) has been deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences (CAS).

3.3 Extraction and isolation

The air-dried fruiting bodies (1100 g) were extracted three times with $CHCl_3$–MeOH (1:1, v/v) at room temperature. After removal of the solvent by evaporation, the residue (44.5 g) was subjected to silica gel column eluted with a petroleum ether–acetone gradient system (1:0–1:1, v/v) to give fractions A–H. Fraction F was subjected to silica gel column eluted with a petroleum ether–acetone gradient system (40:1–10:1, v/v) to give four subfractions: F1–F4. Subfraction F3 was further purified by Sephadex LH-20 using $CHCl_3$–MeOH (1:1, v/v) and on semi-preparative HPLC (MeCN–H_2O, 30/70) to give **1** (3 mg). Fraction G was separated on silica gel using petroleum ether–acetone (3:1, v/v) to afford fractions G1–G4. Fraction G2 was chromatographed on Sephadex LH-20 column eluting with $CHCl_3$–MeOH (1:1, v/v) and then purified on semi-preparative HPLC (MeCN–H_2O, 30/70) to give **2** (1 mg), **3** (2 mg), **4** (8 mg), and **5** (1 mg).

*3.3.1 (1R)-(3-ethenylphenyl)-1,2-ethanediol (**1**)*

Colorless oil; $[\alpha]_D^{18.2}$ −27.7 (*c* 0.08, $CHCl_3$). UV (MeOH) λ_{max}: 208, 248 nm; IR (KBr) ν_{max}: 3407, 2925, 1657, 1604, 1443, 1404, 1076 cm^{-1}; ^1H (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectral data, see Table 1; positive HR-ESI-MS *m/z*: 187.0732 $[M + Na]^+$ (calcd for $C_{10}H_{12}O_2Na$, 187.0734).

*3.3.2 (1R)-(3-formylphenyl)-1,2-ethanediol (**2**)*

Colorless oil; $[\alpha]_D^{21.9}$ −2.1 (*c* 0.16, MeOH). UV (MeOH) λ_{max}: 205 nm; IR (KBr) ν_{max}: 3409, 2926, 2855, 1696, 1605, 1386, 1284, 1075, 696 cm^{-1}; ^1H (600 MHz, MeOD) and ^{13}C NMR (150 MHz, MeOD) spectral data, see Table 1; positive HR-ESI-MS *m/z*: 167.0707 $[M + H]^+$ (calcd for $C_9H_{11}O_3$, 167.0708).

*3.3.3 (1R)-(3-acetophenyl)-1,2-ethanediol (**3**)*

Colorless oil; $[\alpha]_D^{22.2}$ −5.5 (*c* 0.10, MeOH). UV (MeOH) λ_{max}: 205 nm; IR (KBr) ν_{max}: 3416, 2927, 2872, 1725, 1682, 1360, 1278, 1076, 696 cm^{-1}; ^1H (600 MHz, MeOD) and ^{13}C NMR (150 MHz, MeOD) spectral data, see Table 1; positive HR-ESI-MS *m/z*: 203.0685 $[M + H]^+$ (calcd for $C_{10}H_{12}O_3Na$, 203.0684).

3.4 Antibacterial assay

Compounds **1–3** were tested for their antimicrobial activity *in vitro* using the disk-diffusion method as described in the literature with minor modifications [10]. Strains including two species of bacteria (*B. subtilis* ATCC 6633 and *P. aenlgimosa* ATCC 9027) were used. Rifampicin (Sigma Chemical Co.; purity > 97%) was used as positive control (St. Louis, MO, USA). The sterile filter paper disks (6 mm diameter) were soaked in the solution (10 mg/ml) of the test compounds in dimethyl sulfoxide and placed onto nutrient agar medium plates for the test of antibacterial activity. The plates were inoculated with standardized suspension (0.5 unit Mc Farland scale, 0.1 ml) of the tested strains, which were incubated at 37 °C for the test of antibacterial activity. The diameter of the inhibition zone was measured after 18 h.

Acknowledgements

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