Phenylglycol Metabolites from Cultures of the Basidiomycete *Mycena pruinosoviscida* BCC 22723

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Mycenadiols A–D (**1**–**4**, resp.), phenylglycols possessing an ethynyl or vinyl (ethenyl) group were isolated from cultures of the basidiomycete *Mycena pruinosoviscida* BCC 22723. The structures were elucidated on the basis of NMR-spectroscopic and mass spectrometric data. The absolute configurations of **1** and **2** were determined by synthesis. Compounds **1**–**4** are synthetically known, but, they have not been previously isolated from natural sources.

Introduction. – Higher fungi in the genus *Mycena* have been sources of bioactive secondary metabolites with diverse structures such as mycenone (chlorinated benzoquinone derivative; isocitrate lyase inhibitor) from *Mycena* sp. TA 87202 [1], mycenarubins A and B (red pyrroloquinoline alkaloids) from *M. rosea* [2], sanguinones A and B (blue pyrroloquinoline alkaloids) from *M. sanguinolenta* [3], mycenaaurin A (an antibacterial polyene pigment) from *M. aurantiomarginata* [4], cytotoxic strobilurin derivatives from *M. galericulata* [5], and antifungal chlorinated benzoxepine derivatives from *M. galopus* [6][7]. However, many species in this genus still remain chemically unexplored. As part of our search of novel bioactive compounds from fungal sources in Thailand, we have recently been focusing on the structural diversity of the secondary metabolites from cell cultures of basidiomycetes [8–10]. Herein, we report the isolation of phenylglycols mycenadiols A–D (**1**–**4**, resp.) from cultures of *Mycena pruinosoviscida* BCC 22723 (*Fig. 1*). The absolute configurations of the acetylenic compounds **1** and **2** were established by synthesis. To the best of our knowledge, there have been no previous reports on the chemical constituents of natural fruiting bodies or cell cultures of this species.

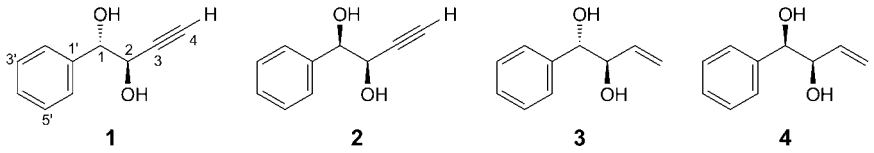

Fig. 1. *Structures of compounds* **1**–**4**

Results and Discussion. – Mycenadiol A (**1**) was isolated as colorless viscous oil. The molecular formula of **1** was established as $C_{10}H_{10}O_2$ on the basis of the sodiated

quasi-molecular-ion peak at *m*/*z* 185.0578 ($C_{10}H_{10}NaO_2^+$; calc. 185.0573) in the HR-ESI-MS. Analysis of the ^{1}H- and ^{13}C-NMR, DEPT-135, and HMQC data revealed that **1** contained a Ph group, two CH–O (δ(C) 76.4 (δ(H) 4.84 (*m*)) and 67.6 (δ(H) 4.53 (*m*))) and a terminal acetylene groups (δ(C) 81.2 (C_q) and 75.9 (δ(H) 2.47 (*m*))). The planar structure was elucidated on the basis of the vicinal and long-range COSY correlations of the signals of H–C(1)/H–C(2) and H–C(2)/H–C(4), respectively, and the HMBCs from H–C(1) to C(2) and C(3), from H–C(2) to C(3) and C(4), and from H–C(4) to C(2) and C(3) indicated the connections from C(1) to C(4). The connection of C(1) to a Ph group (C(1′)) was indicated by the HMBCs from H–C(1) to the Ph C-atoms C(1′) (δ(C) 138.9) and C(2′)/C(6′) (δ(C) 126.8), from H–C(2) to C(1′), and from H–C(2′)/H–C(6′) (δ(H) 7.42 (*m*)) to C(1). To assign the relative configuration, **1** was treated with TsOH · H_2O in 2,2-dimethoxypropane to give the acetonide derivative **5** (*cf. Fig. 2*). NOESY Correlations from both CH–O H-atoms, H–C(1) and H–C(2), to the same acetonide Me (δ(H) 1.49), and the intense cross-peak H–C(1)/H–C(2) indicated that it was a *cis*-acetonide derivative. Therefore, mycenadiol (**1**) was identified as an '*anti*'-diol (*Fig. 2*).

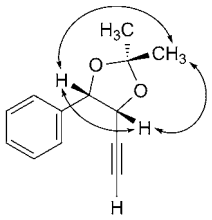

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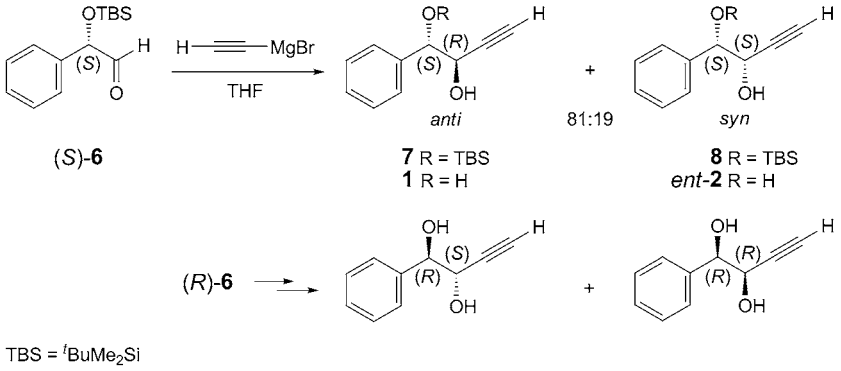
Fig. 2. *NOESY Correlations* (H ↔ H) *of* **5**

The molecular formula of mycenadiol B (**2**) was the same as **1** (HR-ESI-MS). The ^{1}H- and ^{13}C-NMR data were similar to those of **1** with small differences in the chemical shifts of H- and C-atoms. Detailed analysis of the 2D-NMR data revealed the same planar structure with **1**, hence they should be diastereoisomers. The NMR data were consistent with those of the known synthetic compound, (1*S*,2*S*)-1-phenylbut-3-yne-1,2-diol ('*syn*'-isomer), which was previously synthesized in an enantiomerically pure form [11]. However, its optical rotation value has not been reported. The literature search also revealed that a mixture of diastereoisomers of (±)-4-phenylbut-3-yne-1,2-diol was previously synthesized [12], while none of the four diastereoisomers has ever been isolated as a natural product.

To further confirm the structures of **1** and **2**, and to determine the absolute configurations, all diastereoisomers were synthesized (*Scheme*). The reaction of an *O*-protected mandelaldehyde (*S*)-**6** [13] with CH≡CMgBr in THF at 0° gave an 81:19 mixture of diastereoisomeric adducts **7** (*anti*) and **8** (*syn*). These were separated, and each isomer was desilylated (Bu_4NF/THF) to furnish (1*S*,2*R*)-isomer **1** and (1*S*,2*S*)-isomer *ent*-**2**, respectively. Similarly, (1*R*,2*S*)-isomer *ent*-**1** and (1*R*,2*R*)-isomer **2** were synthesized from (*R*)-**6**. The specific rotation of the natural product **1**, $[\alpha]_D^{27} = +27$ ($c = 0.77$, MeOH), was consistent with that of the synthetic (2*S*,3*R*)-isomer **1**, $[\alpha]_D^{25} = +28$ ($c = 0.51$, MeOH), and had the opposite sign of the (2*R*,3*S*)-isomer *ent*-**1**, $[\alpha]_D^{26} = -29$

Scheme. *Synthesis of* **1** *and* **2**, *and Their Enantiomers*



($c = 0.56$, MeOH). The specific rotation of the natural product **2**, $[\alpha]_D^{26} = -12$ ($c = 0.24$, MeOH), was consistent with that of the synthetic (2*R*,3*R*)-isomer **2**, $[\alpha]_D^{25} = -13$ ($c = 1.15$, MeOH), and was the opposite of that of the (2*S*,3*S*)-isomer *ent*-**2**, $[\alpha]_D^{26} = +11$ ($c = 0.63$, MeOH).

Mycenadiols C and D (**3** and **4**, resp.) were elucidated by analysis of NMR and HR-MS data, together with the optical-rotation data. They were identified as the known synthetic compounds, (1*S*,2*R*)-1-phenylbut-3-ene-1,2-diol [14] and (1*R*,2*R*)-1-phenylbut-3-ene-1,2-diol [15], respectively. Compounds **3**, **4**, and their enantiomers have not been previously isolated as natural products.

It should be noted that the structures of mycenadiols A and B (**1** and **2**, resp.), and their diastereoisomers are closely related to a synthetic compound *Centalun*, 2-methyl-1-phenylbut-3-yne-1,2-diol (unspecified configuration), which is a psycholeptic drug with hypnotic and sedative effects [16], but no longer used clinically. The samples of the natural products **1**–**4** and of the synthetic four diastereoisomers, **1**, **2**, *ent*-**1**, and *ent*-**2**, were subjected to several biological-activity tests in our research unit: cytotoxicity against cancer cell lines (KB, MCF-7, and NCI-H187), antimycobacterial activity (*Mycobacterium tuberculosis* H37Ra), antiplasmodial activity (*Plasmodium falciparum* K1), antifungal activity (*Candida albicans*, *Curvularia lunata*, and *Magnaporthe grisea*), and antibacterial activity (*Bacillus cereus*). However, all tested compounds were inactive in these assays at a concentration of 50 μg/ml.

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Experimental Part

General. Column chromatography (CC): silica gel *60 H* (SiO_2; *Merck*) and *Sephadex LH-20* (*GE Healthcare*). Prep. HPLC: *Waters 600* controller, *Waters 2996* photodiode array detector. Optical rotations: *JASCO P-1030* digital polarimeter. UV Spectra: *GBC Cintra 404* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Bruker ALPHA* spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker DRX400* and *AV500D* spectrometers; δ in ppm rel. to Me_4Si as internal standard, J in Hz. HR-ESI-MS: *Bruker micrOTOF* mass spectrometer; in m/z.

Fungal Material. The lignicolous small mushroom used in this study was collected from a leaf litter (unidentified) in Khao Yai National Park, Prachin Buri Province, Thailand, on June 19, 2006. The natural mushroom specimen was deposited with the BIOTEC Bangkok Herbarium as BBH 16990, and the living culture was deposited in the BIOTEC Culture Collection as BCC 22723. On the basis of the morphology of both the macro- and microscopic characteristics, this fungus was identified as *Mycena pruinosoviscida* CORNER of the family *Mycenaceae*. Pileus, 3–12-mm diameter, primrose color when young, then brownish, sometime padi-brown when aged, hemispherical to campanulate, sometime convex to plane, rarely depressed disc, uplifted to revolute, pruinose to granulose, furcate to sulcate, striate, eroded margin, dry, smooth, 2–3-mm context, brownish, moist. Lamellae, decurrent to deeply decurrent, 12–14 lamellulae with two series, thin, narrow; range color lamellae face, from dark brown to creamish at lemellae edge. Stipe, 0.5–1-mm wide × 5–15-mm high, central, cylindrical, fistulose, translucent, color range from primrose at apex to golden honey at the base, or brownish for whole stipe; enlarged at base, slimy cover all stipe.

Fermentation, Extraction, and Isolation. The fungus BCC 22723 was maintained on potato dextrose agar at 25°. The agar was cut into small plugs and inoculated into 3 × 250-ml *Erlenmeyer* flasks containing 25 ml of potato dextrose broth (PDB; potato starch, 4.0 g/l; dextrose, 20.0 g/l). After incubation at 25° for 13 d on a rotary shaker (200 rpm), each primary culture was transferred into a 1000-ml *Erlenmeyer* flask containing 250 ml of the same liquid medium (PDB), and incubated at 25° for 13 d on a rotary shaker (200 rpm). The secondary cultures were pooled, and each 25-ml portion was transferred into 28 × 1000-ml *Erlenmeyer* flasks containing 250 ml of malt extract broth (MEB; malt extract, 6.0 g/l; yeast extract, 1.2 g/l; maltose, 1.8 g/l; dextrose, 6.0 g/l), and the final fermentation was carried out at 25° for 60 d under static conditions. The cultures were filtered to separate broth and mycelia (residue). The broth was extracted with AcOEt (2 × 9 l) and concentrated under reduced pressure to obtain a brown gum (broth extract, 3.4 g). The wet mycelia were macerated in MeOH (1.8 l, r.t., 2 d) and filtered. Hexane (1.8 l) and H_2O (300 ml) were added to the filtrate, and the layers were separated. The H_2O/MeOH (bottom) layer was partially concentrated by evaporation, and the residue was diluted and extracted with AcOEt (2.4 l). The AcOEt layer was concentrated under reduced pressure to obtain a brown gum (mycelial extract, 900 mg). The broth extract (3.4 g) was subjected to CC (SiO_2 (3.7 × 15 cm)); AcOEt/hexane, step gradient elution) to afford 13 fractions, *Frs. 1–13*. *Fr. 9* (40 mg) was further fractionated by CC (SiO_2; AcOEt/hexane 25 : 75), and the fractions were purified by prep. HPLC (reversed-phase column (*Phenomenex Luna 10u C18(2) 100A*, 21.2 × 250 mm, 10 μm)); MeCN/H_2O 20 : 80; flow rate, 8 ml/min) to furnish **3** (t_R 14.2 min; 30 mg). *Fr. 10* (700 mg) was separated by CC (SiO_2; AcOEt/hexane 25 : 75) to afford **3** (135 mg), **4** (91 mg), and **2** (170 mg). *Frs. 11* (1.37 g) and *12* (445 mg) were also submitted to CC (SiO_2; AcOEt/hexane 30 : 70) to give **2** (144 mg) and **1** (750 mg). The mycelial extract (900 mg) was submitted to CC (*Sephadex LH-20*; MeOH; and SiO_2; AcOEt/hexane) to furnish **3** (23 mg), **4** (12 mg), **2** (35 mg), and **1** (94 mg).

(1S,2R)-1-Phenylbut-3-yne-1,2-diol (*Mycenadiol A*; **1**). Colorless oil. $[\alpha]_D^{27} = +27$ ($c = 0.77$, MeOH). $[\alpha]_D^{27} = +63$ ($c = 0.35$, $CHCl_3$). UV (MeOH): 213 (3.46). IR (ATR): 3364, 3289, 1038, 711. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42 (*m*, H–C(2′,6′)); 7.40–7.32 (*m*, H–C(3′,4′,5′)); 4.84 (*m*, H–C(1)); 4.53 (*m*, H–C(2)); 2.47 (*m*, H–C(4)). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.9 (C(1′)); 128.6 (C(3′,4′,5′)); 126.8 (C(2′,6′)); 81.2 (C(3)); 76.4 (C(1)); 75.9 (C(4)); 67.6 (C(2)). HR-ESI-MS: 185.0578 ($[M+Na]^+$, $C_{10}H_{10}NaO_2^+$; calc. 185.0573).

(1R,2R)-1-Phenylbut-3-yne-1,2-diol (*Mycenadiol B*; **2**). Colorless oil. $[\alpha]_D^{26} = -12$ ($c = 0.24$, MeOH). $[\alpha]_D^{27} = -8$ ($c = 0.32$, $CHCl_3$). UV (MeOH): 213 (3.51). IR (ATR): 3378, 3289, 1051, 762, 700. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.43 (*m*, H–C(2′,6′)); 7.37 (*m*, H–C(3′,5′)); 7.34 (*m*, H–C(4′)); 4.73 (*d*, $J = 6.9$, H–C(1)); 4.41 (*m*, H–C(2)); 2.93 (br. *s*, HO–C(1)); 2.69 (br. *d*, $J = 5.1$, HO–C(2)); 2.45 (*d*, $J = 2.1$, H–C(4)). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.9; 128.5; 128.3; 127.1; 81.6; 77.1; 75.2; 67.1. HR-ESI-MS: 185.0579 ($[M+Na]^+$, $C_{10}H_{10}NaO_2^+$; calc. 185.0573).

(1S,2R)-1-Phenylbut-3-ene-1,2-diol (*Mycenadiol C*; **3**). Colorless oil. $[\alpha]_D^{24} = +57$ ($c = 0.16$, MeOH). $[\alpha]_D^{27} = +63$ ($c = 0.21$, $CHCl_3$) ([14]: $[\alpha]_D^{20} = +75.8$ ($c = 0.96$, $CHCl_3$)). UV MeOH): 215 (3.56). IR (ATR): 3378, 1029, 726, 700. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.35 (*m*, H–C(2′,6′;3′,5′)); 7.31 (*m*, H–C(4′)); 5.82 (*ddd*, $J = 17.3, 10.5, 6.1$, H–C(3)); 5.29 (*d*, $J = 17.3$, H_a–C(4)); 5.23 (*d*, $J = 10.5$, H_b–C(4)); 4.77 (*d*, $J = 4.8$, H–C(1)); 4.32 (*dd*, $J = 6.1, 4.8$, H–C(2)). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.0 (C(1′));

136.1 (C(3)); 128.6 (C(3′,5′)); 128.2 (C(4′)); 126.9 (C(2′,6′)); 118.1 (CH_2(4)); 76.9 (C(2)); 76.7 (C(1)). HR-ESI-MS: 187.0735 ($[M+Na]^+$, $C_{10}H_{12}NaO_2^+$; calc. 187.0730).

(1R,2R)-1-Phenylbut-3-ene-1,2-diol (*Mycenadiol D*; **4**). Colorless oil. $[\alpha]_D^{27} = +13$ ($c = 0.29$, MeOH). $[\alpha]_D^{27} = -3$ ($c = 0.13$, $CHCl_3$) ([15]: $[\alpha]_D^{25} = -4.2$ ($c = 0.66$, $CHCl_3$)). UV (MeOH): 214 (3.55). IR (ATR): 3385, 995, 765, 700. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.36–7.34 (*m*, H–C(2′,6′;3′,5′)); 7.31 (*m*, H–C(4′)); 5.73 (*ddd*, $J = 17.3$, 10.6, 5.5, H–C(3)); 5.26 (*dt*, $J = 17.3$, 1.4, H_a–C(4)); 5.15 (*dt*, $J = 10.6$, 1.4, H_b–C(4)); 4.50 (*d*, $J = 8.9$, H–C(1)); 4.23 (*ddt*, $J = 8.9$, 5.5, 1.4, H–C(2)). ^{13}C-NMR (125 MHz, $CDCl_3$): 140.2 (C(1′)); 136.3 (C(3)); 128.4 (C(3′,5′)); 128.1 (C(4′)); 127.0 (C(2′,6′)); 117.1 (CH_2(4)); 77.6 (C(1)); 76.9 (C(2)). HR-ESI-MS: 187.0732 ($[M+Na]^+$, $C_{10}H_{12}NaO_2^+$; calc. 187.0730).

Synthesis of the Acetonide Derivative **5**. To a soln. of **1** (32 mg) in 2,2-dimethoxypropane (1.5 ml) was added $TsOH \cdot H_2O$ (*ca.* 2 mg), and the mixture was stirred at r.t. for 2 h. The reaction was quenched by addition of 1M aq. $NaHCO_3$ soln. (2 ml), and the mixture was extracted with AcOEt. The org. layer was dried ($MgSO_4$) and concentrated *in vacuo* to furnish **5** (21 mg, 53%). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.43 (*m*, H–C(2′,6′)); 7.37 (*m*, H–C(3′,5′)); 7.34 (*m*, H–C(4′)); 5.24 (*d*, $J = 6.0$, H–C(1)); 5.01 (*dd*, $J = 6.0$, 2.2, H–C(2)); 2.29 (*d*, $J = 2.2$, H–C(4)); 1.71 (*s*, Me); 1.49 (*s*, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.1 (C(1′)); 128.5 (C(4′)); 128.3 (C(3′,5′)); 127.2 (C(2′,6′)); 100.7 (Me^2C); 80.4 (C(1)); 80.1 (C(3)); 77.2 (C(4)); 70.8 (C(2)); 27.7 (Me); 26.2 (Me). HR-ESI-MS: 225.0885 ($[M+Na]^+$, $C_{13}H_{14}NaO_2^+$; calc. 225.0886).

Synthesis of Compounds **7** *and* **8**. To a stirred soln. of CH≡CMgBr (23.2 ml, 0.5M in THF, 11.6 mmol) at 0° was added a soln. of aldehyde (*S*)-**6** (1.45 g, 5.79 mmol) in THF (6 ml) dropwise during 3 min, and the mixture was stirred for 1 h. The reaction was quenched by addition of aq. sat. NH_4Cl soln. (1.2 ml). The ice-water bath was removed, and the mixture was diluted with Et_2O (20 ml), dried ($MgSO_4$), and then filtered. The filtrate was concentrated under reduced pressure to leave pale-brown oil (1.73 g), which was subjected to CC (SiO_2; AcOEt/hexane, from 2:98 to 5:95) to give **7** (1.07 g, 67%) and **8** (256 mg, 16%).

*(1S,2R)-1-{[(*tert*-Butyl)(dimethyl)silyl]oxy}-1-phenylbut-3-yn-2-ol* (**7**). Colorless oil. IR (ATR): 3311, 1255, 1104, 838, 778, 700. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.40 (*m*, 2 arom. H); 7.35–7.29 (*m*, 3 arom. H); 4.78 (*d*, $J = 4.7$, H–C(1)); 4.39 (*dd*, $J = 4.7$, 2.2, H–C(2)); 2.40 (*d*, $J = 2.2$, H–C(4)); 0.92 (*s*, ^{t}Bu); 0.08 (*s*, Me); −0.10 (*s*, Me). HR-ESI-MS: 299.1441 ($[M+Na]^+$, $C_{16}H_{24}NaO_2Si^+$; calc. 299.1438).

*(1S,2S)-1-{[(*tert*-Butyl)(dimethyl)silyl]oxy}-1-phenylbut-3-yn-2-ol* (**8**). Colorless oil. IR (ATR): 3298, 1255, 1097, 837, 779, 700. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.37–7.29 (*m*, 5 arom. H); 4.69 (*d*, $J = 6.2$, H–C(1)); 4.31 (*dd*, $J = 6.2$, 2.1, H–C(2)); 2.80 (br. *s*, HO–C(2)); 2.38 (*d*, $J = 2.1$, H–C(4)); 0.91 (*s*, ^{t}Bu); 0.09 (*s*, Me); −0.13 (*s*, Me). HR-ESI-MS: 299.1435 ($[M+Na]^+$, $C_{16}H_{24}NaO_2Si^+$; calc. 299.1438).

Synthesis of **1** *and* ent-**2**. To a stirred soln. of **7** (940 mg, 3.40 mmol) in THF (7 ml) at 0° was added a soln. of Bu_4NF (6.8 ml, 1.0M in THF, 6.8 mmol) dropwise during 5 min, and the mixture was stirred at 0° for 30 min, then at r.t. for 2 h. The reaction was quenched by addition of sat. aq. NH_4Cl soln. (15 ml) at 0°. The mixture was diluted with AcOEt, the org. layer was separated, and the aq. layer was extracted with AcOEt (2×20 ml). The combined org. extracts were dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by CC (SiO_2; MeOH/CH_2Cl_2, from 0:100 to 3:97) to give **1** (528 mg, 96%; $[\alpha]_D^{25} = +28$ ($c = 0.51$, MeOH)). By a similar procedure, compound **8** was desilylated to give *ent*-**2**, ^{1}H- and ^{13}C-NMR data of which were consistent with those reported in [8].

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