# Five Aromatics Bearing a 4-*O*-Methylglucose Unit from *Cordyceps cicadae*

by **Shu-Wei Zhang** and **Li-Jiang Xuan***

State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Science, 555 Zuchongzhi Road, Zhangjiang Hi-Tech Park, Shanghai 201203, P. R. China (phone: +86-21-50272221; e-mail: ljxuan@mail.shcnc.ac.cn)

Five new aromatics bearing a 4-*O*-methylglucose unit, namely 3-methoxy-1,4-hydroquinone 1-(4′-*O*-methyl-β-glucopyranoside) (=4-hydroxy-3-methoxyphenyl 4-*O*-methyl-β-glucopyranoside; **1**), 3-methoxy-1,4-hydroquinone 4-(4′-*O*-methyl-β-glucopyranoside) (=4-hydroxy-2-methoxyphenyl 4-*O*-methyl-β-glucopyranoside; **2**), vanillic acid 4-(4′-*O*-methyl-β-glucopyranoside) (=3-methoxy-4-[(*O*-methyl-β-glucopyranosyl)oxy]benzoic acid; **3**), 5-methoxycinnamic acid 3-*O*-(4′-*O*-methyl-β-glucopyranoside) (=(2*E*)-3-{3-methoxy-5-[(4-*O*-methyl-β-glucopyranosyl)oxy]phenyl}prop-2-enoic acid; **4**), and naphthalene-1,8-diol 1,8-bis(4′-*O*-methyl-β-glucopyranoside) (=naphthalene-1,8-diyl bis(4-*O*-methyl-β-glucopyranoside; **5**), were isolated from the cultivated *Cordyceps cicadae* mycelia, together with thirteen known compounds. Their structures were determined by spectroscopic methods. The absolute configurations of the sugar units were not determined.

**Introduction.** – *Cordyceps cicadae*, belonging to the genus *Cordyceps* (family Clavicipitaceae, Ascomycotina), is a major parasitic fungus growing on the larvae of *Cicada flammata*, *Platypleura kaempferi*, *Crytotympana pustulata*, or *Platylomia pieli*. It has been known and used in traditional Chinese medicine (TCM) for about 1000 years. Its putative active functions include: *1*) treatment of childhood convulsion and palpitation, *2*) antitumor activity, *3*) relief of palpitations, *4*) enhancement of blood aggregation, and *5*) analgetic and sedative activity [1]. *Jin et al.* found that *Cordyceps cicadae* could prevent the progression of chronic renal failure (CRF) in the rat glomerulosclerosis model [2]. The following chemical constituents have been isolated from *Cordyceps cicadae:* polysaccharides [3], galactomannan [4], cordycepin, adenosine [5], and ISP-1(myriocin) [6].

Compounds possessing a 4-*O*-methylglucose moiety have seldom been found in natural sources, except in some insect pathogenic fungi [7][8]. Herein, we report the isolation and structural elucidation of the new aromatic 4-*O*-methylglucosides **1**–**5** from cultivated *Cordyceps cicadae* mycelia. Their structures were established by spectroscopic methods, especially 2D-NMR and MS analyses. Also isolated were thirteen known compounds, namely adenosine, $N^6$-(2-hydroxyethyl)adenine, $N^6$-(2-hydroxyethyl)adenosine [5], guanosine, guanine [9], uracil, uridine [9][10], thymidine [10][11], 2-deoxyadenosine [12], 5-(3-hydroxybutyl)furan-2-acetic acid [13], mevalonolactone [14], (3β,5α,8α,24*R*)-5,8-epidioxy-24-methylcholesta-6,22-dien-3-yl glucopyranoside, and (3β,24*R*)-5,6-epoxy-24-methylcholesta-7,22-dien-3-ol [15], which were

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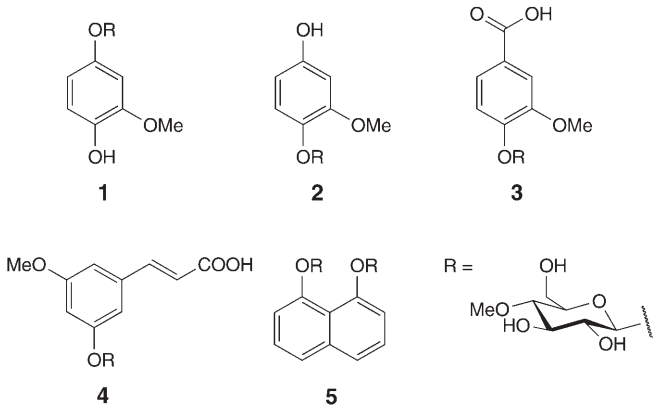
identified by comparison of spectroscopic data and by co-elution with authentic samples on TLC.

**Results and Discussion.** – The cultivated mycelia of *Cordyceps cicadae* (4.0 kg) were extracted three times with 70% (*v*/*v*) aqueous ethanol at room temperature. The combined extracts were evaporated to give a deep-brown syrup, which was extracted with $CHCl_3$ and then BuOH. The BuOH extract and aqueous solution were repeatedly subjected to column chromatography to afford the five new aromatics **1**–**5** bearing a 4-*O*-methyglucose unit and other known compounds.




Compound **1** was obtained as a white amorphous powder. Its molecular formula was deduced as $C_{14}H_{20}O_8$ from the $[M+Na]^+$ ion peak at 339.1053 in the HR-ESI-MS. The IR spectrum revealed the presence of OH groups (3363 $cm^{-1}$) and of a benzene ring (1633 and 1518 $cm^{-1}$). Compound **1** was elucidated as 3-methoxy-1,4-hydroquinone 1-(4′-*O*-methyl-*β*-glucopyranoside)[1]).

The $^1$H-NMR spectra of **1** (*Table 1*) showed the signals of a 1,2,4-trisubstituted benzene moiety ($\delta$(H) 6.86 (*d*, *J* = 8.8 Hz, 1 H), 6.85 (*d*, *J* = 2.9 Hz, 1 H), 6.66 (*dd*, *J* = 2.8, 8.8 Hz, 1 H)). This was consistent with the $^{13}$C-NMR spectrum showing six aromatic C-atoms from $\delta$(C) 104.3 to 152.1, including three CH groups and three oxygenated quaternary C-atoms (*Table 1*). The HMBC correlation from the protons at $\delta$(H) 3.86 of one MeO group ($\delta$(C) 57.2) to C(3) ($\delta$(C) 149.3) indicated that this MeO group was attached to C(3) of the aglycone (*Fig.*). The aglycone structure was established by the HMBC correlations from H–C(2) ($\delta$(H) 6.85 (*d*, *J* = 2.9 Hz)) to C(4) ($\delta$(C) 142.0) and C(6) ($\delta$(C) 110.2), from H–C(5) ($\delta$(H) 6.86 (*d*, *J* = 8.8 Hz)) to C(1) ($\delta$(C) 152.1) and C(3) ($\delta$(C) 149.3), and from H–C(6) ($\delta$(H) 6.66 (*dd*, *J* = 2.8, 8.8 Hz)) to C(1) ($\delta$(C) 152.1) and C(4) ($\delta$(C) 142.0). Hence, the aglycone was elucidated as a methoxyhydroquinone. These data of the aglycone of **1** were consistent with the reported data of tachioside [16]. The remaining seven C-atoms, including one MeO group at $\delta$(C) 61.3 ($\delta$(H) 3.59 (*s*)), were classified as those of a sugar unit. The anomeric H-atom resonated at $\delta$(H) 4.94 (*d*, *J* = 7.8 Hz) and the anomeric C-atom at $\delta$(C) 102.7. The large coupling constant of the anomeric H-atom (*J* = 7.8 Hz) suggested a *β*-configured Glc unit. The connectivity from C(1′) to C(6′) was elucidated by analyses of $^1$H-NMR, COSY, and HMQC data. The HMBC correlation from the protons at $\delta$(H) 3.59 (*s*) of MeO ($\delta$(C) 61.3) to C(4′) ($\delta$(C) 80.6) indicated that the OH group at C(4′) was methylated. The coupling constants $J(1',2') = 7.8$, $J(2',3') = 9.4$, $J(3',4') = 9.3$, and $J(4',5') = 9.6$ Hz placed all the involved protons in

[1]) Arbitrary atom numbering or name; for systematic names, see *Exper. Part.*

Table 1. *$^1$H- and $^{13}$C-NMR Data of* **1**–**3**[1]). At 300 ($^1$H) and 400 MHz ($^{13}$C), resp.; $\delta$ in ppm, $J$ in Hz[a]).

| | **1**[b]) | | **2**[b]) | | **3**[c]) | |
|---|---|---|---|---|---|---|
| | $\delta$(H) | $\delta$(C) | $\delta$(H) | $\delta$(C) | $\delta$(H) | $\delta$(C) |
| C(1) | | 152.1 | | 154.9 | | 124.5 |
| H–C(2) | 6.85 (*d*, *J* = 2.9) | 104.3 | 6.61 (*d*, *J* = 2.7) | 103.6 | 7.48 (*d*, *J* = 1.7) | 112.7 |
| C(3) | | 149.3 | | 152.8 | | 148.4 |
| C(4) | | 142.0 | | 142.0 | | 150.0 |
| H–C(5) | 6.86 (*d*, *J* = 8.8) | 116.8 | 7.06 (*d*, *J* = 8.8) | 120.9 | 7.15 (*d*, *J* = 8.5) | 114.1 |
| H–C(6) | 6.66 (*dd*, *J* = 2.8, 8.8) | 110.2 | 6.45 (*dd*, *J* = 2.7, 8.8) | 109.4 | 7.50 (*dd*, *J* = 1.7, 8.5) | 122.6 |
| MeO | 3.86 (*s*) | 57.2 | 3.85 (*s*) | 58.4 | 3.81 (*s*) | 55.5 |
| COOH | | – | | – | | 167.9 |
| H–C(1′) | 4.94 (*d*, *J* = 7.8) | 102.7 | 4.88 (*d*, *J* = 7.8) | 104.5 | 5.05 (*d*, *J* = 7.8) | 99.1 |
| H–C(2′) | 3.53 (*dd*, *J* = 7.9, 9.4) | 74.4 | 3.55 (*dd*, *J* = 7.8, 9.3) | 75.8 | 3.31 (overlapped in $H_2O$) | 73.2 |
| H–C(3′) | 3.67 (*t*, *J* = 9.3) | 76.7 | 3.65 (*t*, *J* = 9.2) | 78.1 | 3.38–3.41 (*m*) | 76.4 |
| H–C(4′) | 3.28 (*dd*, *J* = 9.4, 9.6) | 80.6 | 3.30 (*t*, *J* = 9.7) | 81.7 | 3.05 (*t*, *J* = 9.3) | 78.8 |
| H–C(5′) | 3.54–3.58 (*m*) | 76.5 | 3.48 (*ddd*, *J* = 2.1, 4.8, 9.8) | 77.8 | 3.38–3.41 (*m*) | 75.6 |
| H–C(6′) | 3.92 (*dd*, *J* = 2.1, 12.4), 3.76 (*dd*, *J* = 5.4, 12.4) | 61.7 | 3.85–3.91 (*m*), 3.75 (*dd*, *J* = 4.8, 12.5) | 62.9 | 3.61 (*dd*, *J* = 3.6, 11.8), 3.49 (*dd*, *J* = 4.9, 11.8) | 60.1 |
| 4′-MeO | 3.59 (*s*) | 61.3 | 3.59 (*s*) | 62.6 | 3.46 (*s*) | 59.6 |

[a]) In case of overlapping signals, no multiplicities are given. [b]) Measured in $CD_3OD$. [c]) Measured in ($D_6$)DMSO.

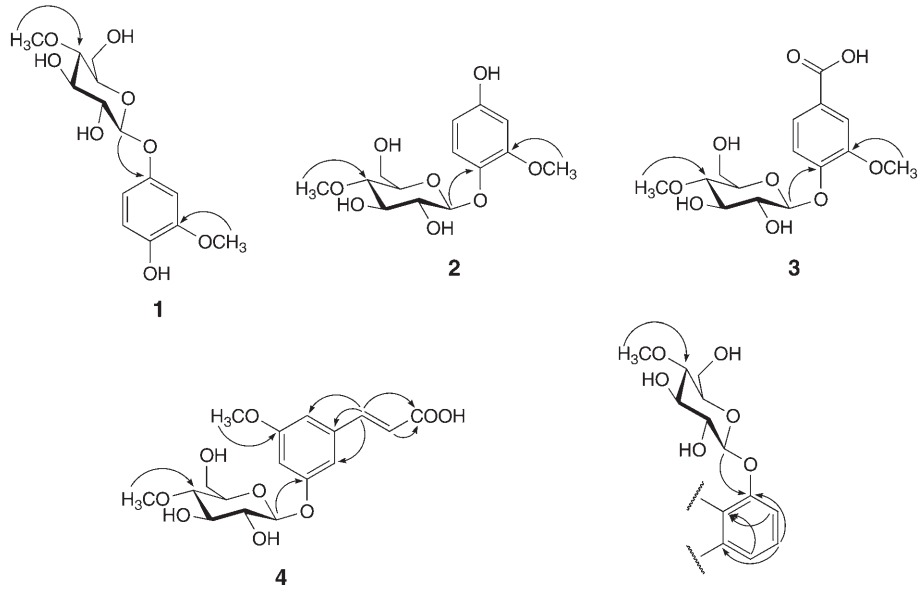



Figure. *Key HMBC* (H → C) *correlations for* **1**–**5**

axial orientation at a pyranose ring. Therefore, the sugar unit was identified as 4-*O*-methyl-$\beta$-glucopyranose. In the ESI-MS spectrum of **1**, the $[M - C_7H_{13}O_5]^-$ ion peak at *m/z* 139.1 also supported the presence of a methoxyglucose unit in compound **1**. The intense HMBC correlation from H–C(1′) to C(1) of the aglycone clearly indicated the connectivity between the sugar unit and the aglycone (*Fig.*).

Compound **2** had the molecular formula $C_{14}H_{20}O_8$, as determined by HR-ESI-MS (*m/z* 339.1072 ($[M + Na]^+$)), similar to that of **1**. Analogous $^1$H- and $^{13}$C-NMR spectra of **1** and **2** (*Table 1*) indicated that compound **2** also contains a 4-*O*-methyl-$\beta$-glucose unit and a methoxyhydroquinone moiety. The only difference between them was the position at which the Glc unit was attached to the aglycone. The Glc unit was connected to C(4) of the aglycone in **2**, which was confirmed by the HMBC correlation from the anomeric H-atom at $\delta$(H) 4.88 (*d*, $J = 7.8$ Hz) to C(4) ($\delta$(C) 142.0) (*Fig.*). Therefore the structure of **2** was determined as 2-methoxy-1,4-hydroquinone 4-(4′-*O*-methyl-$\beta$-glucopyranoside)[1]).

Compound **3** was obtained as a white amorphous powder. A HR-ESI-MS (positive mode) showed the $[M + H]^+$ ion peak at *m/z* 345.1196, in accord with the molecular formula $C_{15}H_{20}O_9$, and supported by the $^1$H- and $^{13}$C-NMR data (*Table 1*). Compound **3** was determined as vanillic acid 4-(4′-*O*-methyl-$\beta$-glucopyranoside)[1]).

The $^1$H-NMR spectrum of **3** in ($D_6$)DMSO (*Table 1*) exhibited the characteristic pattern of a 1,2,4-trisubstituted benzene moiety ($\delta$(H) 7.50 (*d*, $J = 1.7$, 8.5 Hz, 1 H), 7.48 (*d*, $J = 1.7$ Hz, 1 H), 7.15 (*d*, $J =$ 8.5 Hz, 1 H)), two MeO ($\delta$(H) 3.81 (*s*, 3 H), 3.46 (*s*, 3 H)), and a Glc unit, the anomeric H-atom resonating at $\delta$(H) 5.05 (*d*, $J = 7.8$ Hz). Fifteen signals were observed in the $^{13}$C-NMR spectrum in ($D_6$)DMSO (*Table 1*), with two MeO, one oxygenated $CH_2$, five oxygenated $sp^3$ CH, and three $sp^2$ CH groups, three quaternary $sp^2$ C-atoms, and one carboxy C-atom ($\delta$(C) 167.9). The aglycone was characterized as vanillic acid (=4-hydroxy-3-methoxybenzoic acid) from the HMBC correlations from H–C(2) ($\delta$(H) 7.48 (*d*, $J = 1.7$ Hz)) to C(6) ($\delta$(C) 122.6), C(4) ($\delta$(C) 150.0), and carboxy C-atom ($\delta$(C) 167.9), from H–C(5) ($\delta$(H) 7.15 (*d*, $J = 8.5$ Hz)) to C(1) ($\delta$(C) 124.5) and C(3) ($\delta$(C) 148.4), from H–C(6) ($\delta$(H) 7.50 (*dd*, $J = 1.7$, 8.5 Hz)) to C(2) ($\delta$(C) 112.7), C(4) ($\delta$(C) 150.0), and carboxy C-atom ($\delta$(C) 167.9), and from the protons at $\delta$(H) 3.81 (*s*) of MeO ($\delta$(C) 55.5) to C(3) ($\delta$(C) 148.4) (*Fig.*). The NMR data of the aglycone of **3** were consistent with those of 4-hydroxy-3-methoxybenzoic acid reported by *Scott* [17]. The presence of the 4-*O*-methyl-$\beta$-glucose unit was determined by the analyses of the $^1$H- and $^{13}$C-NMR, COSY, HMBC, and ESI-MS data. Furthermore, the HMBC correlation from the anomeric proton of the 4′-*O*-methylglucose to C(4) ($\delta$(C) 150.0) of the aglycone clearly indicated the connective position between the Glc unit and the aglycone.

Compound **4** was obtained as a white amorphous powder. The HR-ESI-MS showed the $[M + Na]^+$ ion peak at *m/z* 393.1191 (calc. 393.1162), corresponding to the molecular formula $C_{17}H_{22}O_9$. Its IR spectrum revealed a broad OH absorption centered at 3378 cm$^{-1}$ and absorptions at 1695 and 1635 cm$^{-1}$ due to an $\alpha,\beta$-unsaturated carboxy group as well as phenyl absorptions at 1598 and 1513 cm$^{-1}$. On the basis of the spectral analyses, compound **4** was determined as 5-methoxycinnamic acid 3-(4′-*O*-methyl-$\beta$-glucopyranoside)[1]).

The $^1$H-NMR spectrum of **4** (*Table 2*) exhibited three *meta*-related proton *s* at $\delta$(H) 7.24 (1 H) and 7.16 (2 H), two *trans*-olefinic-proton *d* at $\delta$(H) 7.61 ($J = 15.9$ Hz) and 6.38 ($J = 15.9$ Hz), two MeO *s* at $\delta$(H) 3.89 and 3.58, and the characteristic signals of a 4′-*O*-methylglucose unit, the anomeric H-atom resonating at $\delta$(H) 4.96 (*d*, $J = 7.5$ Hz) indicating $\beta$-configuration. These data, supported by the $^{13}$C-NMR, DEPT, HMQC, COSY, HMBC, and ESI-MS data, were consistent with a cinnamic acid

Table 2. *$^1$H- and $^{13}$C-NMR Data of* **4** *and* **5**[1])At 300 ($^1$H) and 400 MHz ($^{13}$C), resp.; $\delta$ in ppm, $J$ in Hz[a]).

| | **4**[b]) | | **5**[c]) | |
|---|---|---|---|---|
| | $\delta$(H) | $\delta$(C) | $\delta$(H) | $\delta$(C) |
| C(1) | | 130.9 | | 155.6 |
| H–C(2) | 7.24 (*s*) | 112.8 | 7.57 (*d*, *J* = 6.3) | 125.7 |
| C(3) or H–C(3) | | 150.0 | 7.44 (*dd*, *J* = 6.6, 7.1) | 129.4 |
| H–C(4) | 7.16 (*s*) | 117.5 | 7.21 (*d*, *J* = 7.1) | 113.5 |
| C(5) or H–C(5) | | 151.1 | 7.21 (*d*, *J* = 7.1) | 113.5 |
| H–C(6) | 7.16 (*s*) | 123.8 | 7.44 (*dd*, *J* = 6.6, 7.1) | 129.4 |
| H–C(7) | 7.61 (*d*, *J* = 15.9) | 146.5 | 7.57 (*d*, *J* = 6.3) | 125.7 |
| H–C(8) or C(8) | 6.38 (*d*, *J* = 15.9) | 118.2 | | 155.6 |
| C(9) | | 171.2 | | 119.7 |
| C(10) | | – | | 139.5 |
| MeO | 3.89 (*s*) | 57.1 | | – |
| H–C(1′) | 4.96 (*d*, *J* = 7.5) | 102.2 | 5.25 (*d*, *J* = 7.8) | 103.6 |
| H–C(2′) | 3.54 (*dd*, *J* = 7.4, 9.3) | 75.1 | 3.75–3.77 (*m*) | 76.1 |
| H–C(3′) | 3.60 (*dd*, *J* = 8.5, 9.3) | 77.9 | 3.71–3.77 (*m*) | 77.9 |
| H–C(4′) | 3.23 (*dd*, *J* = 8.7, 9.7) | 80.8 | 3.39 (*dd*, *J* = 8.8, 9.4) | 81.7 |
| H–C(5′) | 3.45 (*ddd*, *J* = 2.1, 4.7, 9.8) | 77.4 | 3.66–3.69 (*m*) | 78.0 |
| $CH_2$(6′) | 3.84 (*dd*, *J* = 2.1, 12.2), | 62.2 | 3.96 (*d*, *J* = 11.9), | 63.0 |
| | 3.70 (*dd*, *J* = 4.8, 12.2) | | 3.80 (*dd*, *J* = 5.2, 11.9) | |
| 4′-MeO | 3.58 (*s*) | 61.3 | 3.63 (*s*) | 62.8 |

[a]) In case of overlapping signals, no multiplicities are given. [b]) Measured in $CD_3OD$. [c]) Measured in $D_2O$.

bearing one MeO and one (4-*O*-methyl-$\beta$-glycopyranosyl)oxy substituent (*Table 2*). The HMBC spectrum showed a correlation between the anomeric proton of the modified Glc unit to C(3) ($\delta$(C) 150.0) of the aglycone, which indicated that the Glc unit was connected to C(3) of the alycone) (*Fig.*).

Compound **5**, obtained as a yellow amorphous powder, was assigned the molecular formula $C_{24}H_{32}O_{12}$, as determined from the $[M + Na]^+$ peak at $m/z$ 535.1780 in the HR-ESI-MS. Thirteen signals were observed in the $^{13}$C-NMR spectrum of **5**, namely of one MeO, one oxygenated $CH_2$, five oxygenated $sp^3$ CH, and three $sp^2$ CH groups, of two quaternary $sp^2$ C-atoms, and of one oxygenated quaternary $sp^2$ C-atom (*Table 2*). These data suggested a $C_2$ axis of symmetry or – less likely – a plane of symmetry (*SE*) within the structure of compound **5**. Compound **5** was characterized as naphthalene-1,8-diol 1,8-bis(4′-*O*-methyl-$\beta$-glucopyranoside)[1]).

The $^1$H-NMR spectrum of **5** (*Table 2*) exhibited the characteristic pattern of a 1,2,3-trisubstituted aromatic ring ($\delta$(H) 7.57 (*d*, *J* = 6.3 Hz), 7.44 (*t*, *J* = 6.6, 7.1 Hz), 7.21 (*d*, *J* = 7.1 Hz)), supported by the $^1$H,$^1$H-COSY data. The $^1$H- and $^{13}$C-NMR, COSY, HMBC, and ESI-MS data confirmed the presence of a 4-*O*-methyl-$\beta$-glucopyranosyl unit in **5**, like in compounds **1**–**4**, the anomeric H-atom resonating at $\delta$(H) 5.25 (*d*, *J* = 7.8 Hz) and the anomeric C-atom resonating at $\delta$(C) 103.6. The partial structure **A** (*Fig.*) was established by the HMBC correlations from H–C(3) ($\delta$(H) 7.44 (*t*, *J* = 6.6, 7.1 Hz)) to C(1) ($\delta$(C) 155.6) and C(10) ($\delta$(C) 139.5), from H–C(2) ($\delta$(H) 7.57 (*d*, *J* = 6.3 Hz)) and H–C(4) ($\delta$(H) 7.21 (*d*, *J* = 7.1 Hz)) to C(9) ($\delta$(C) 119.7), and from the anomeric proton of the Glc unit to C(1) of the aglycone. Taking into account the molecular formula $C_{24}H_{32}O_{12}$, the aglycone of **5** was characterized as naphthalene-1,8-diol, and **5** was assigned as a naphthalenediol diglycoside. The data of the aglycone were consistent with those of the naphthalene moiety of Sch 49209 reported by *Chu et al.* [18].

We would like to thank Dr. *Zhu-An Chen*, Insitute of Subtropocal Crops, Zhejiang Academy of Sciences, for providing the cultivated *Cordyceps cicadae* mycelia.

## Experimental Part

*General.* Column chromatography (CC): *MCI-CHP20P* gel (75–150 μm; *Mitsubishi Chemical Industries Co., Ltd.*), *HW-40F* (30–60 μm; *Tosoh Co., Ltd.*), and silica gel *H* (10–40 μm, *Qingdao Haiyang Chemical Co., Ltd.*). TLC: silica gel $GF_{254}$; visualization under UV light, with $I_2$ vapor, or by spraying anisaldehyde/sulfuric acid reagent. UV Spectra: *Shimadazu UV-2450* spectrophotometer; $\lambda_{max}$ ($\log \varepsilon$) in nm. IR Spectra: *Hitachi 275-50* spectrometer; in $cm^{-1}$. $^1H$- and $^{13}C$-NMR, COSY, HMQC, HMBC: *Bruker DRX-400* spectrometer; $\delta$ in ppm, *J* in Hz. ESI- and HR-ESI-MS: *Finnigan LCQ-DECA* spectrometer; in *m*/*z*.

*Fungal Material. Paecilomyces cicadae* (MIQUEL) SAMSON was collected from Xikou Forest, Zhejiang Province, China, on *Platylomia Pieli* KATO, and identified by Dr. *Zhu-An Chen* of the Biotechnology Research Unit, Institute of Subtropical Crops, Zhejiang Academy of Sciences. A voucher specimen (No. APC-20) was deposited at the Institute of Subtropical Crops, Zhejiang Academy of Sciences.

*Cultivation of Fungi.* The hard-boiled wheat was moist-heat sterilized for 40 min. The culture of *Paecilomyces cicadae* was incubated on potato sucrose agar slants for 3 days (at 21°), then transferred into the wheat culture medium. The culture was subsequently incubated (at 21°) for 30 days, then harvested for further study.

*Extraction and Isolation.* The cultivated mycelia of *Cordyceps cicadae* (4.0 kg) were extracted three times with 70% (*v*/*v*) aq. ethanol at r.t. The combined extracts were concentrated to give a deep-brown syrup, which was extracted with $CHCl_3$, then with BuOH. The $CHCl_3$ extract was subjected to CC ($SiO_2$) to provide three known compounds, mevalonolactone, (3*β*,24*R*)-5,6-epoxy-24-methylcholesta-7,22-dien-3-ol, and (3*β*,5*α*,8*α*,24*R*)-5,8-epidioxy-24-methylcholesta-6,22-dien-3-yl glucopyranoside. The BuOH extract (30 g) was subjected to CC (*MCI* gel; MeOH/$H_2O$ gradient): *Fr. A.1–A.3*. *Fr. A.1* was subjected to CC (*HW-40F*; $H_2O$): **1** (10 mg) and **2** (4 mg). *Fr. A.2* was subjected to CC (*HW-40F*; $H_2O$): **4** (13 mg). *Fr. A.3* was subjected to CC (*HW-40F*; $H_2O$): **5** (18 mg). The aq. soln. was subjected to CC (*MCI* gel; MeOH/$H_2O$ gradient): *Fr. B.1–B.5*. *Fr. B.2* was repeatedly purified by CC (*MCI* gel; MeOH/$H_2O$ 2:8) and CC (*HW-40F*; $H_2O$) to afford **3** (12 mg). *Fr. B.1* and *B.3–B.5* were repeatedly subjected to CC (*MCI* gel, *HW-40F*) to yield other known compounds.

*3-Methoxy-1,4-hydroquinone 1-(4′-*O*-methyl-β-glucopyranoside)* (=*4-Hydroxy-3-methoxyphenyl 4-*O*-Methyl-β-glucopyranoside*; **1**): White, amorphous powder. UV (MeOH): 280 (3.30), 225 (3.68). IR (KBr): 3363, 1633, 1518, 1085. $^1H$- and $^{13}C$-NMR: *Table 1*. ESI-MS (pos.): 655.1 ($[2M+Na]^+$), 339.1 ($[M+Na]^+$). ESI-MS (neg.): 315.2 ($[M-H]^-$), 139.1 ($[M-C_7H_{13}O_5]^-$). HR-ESI-MS (pos.): 339.1053 ($[M+Na]^+$, $C_{14}H_{20}O_8Na^+$; calc. 339.1056).

*3-Methoxy-1,4-hydroquinone 4-(4′-*O*-methyl-β-glucopyranoside)* (=*4-Hydroxy-2-methoxyphenyl 4-*O*-Methyl-β-glucopyranoside*; **2**): White, amorphous powder. UV (MeOH): 280 (3.28), 225 (3.70). IR (KBr): 3365, 1617, 1517, 1085. $^1H$- and $^{13}C$-NMR: *Table 1*. ESI-MS (pos.): 339.2 ($[M+Na]^+$). ESI-MS (neg.): 631.2 ($[2M-H]^-$), 315.0 ($[M-H]^-$), 139.0 ($[M-C_7H_{13}O_5]^-$). HR-ESI-MS (pos.): 339.1072 ($[M+Na]^+$, $C_{14}H_{20}O_8Na^+$; calc. 339.1056).

*Vanillic Acid 4-(4′-*O*-methyl-β-glucopyranoside)* (=*3-Methoxy-4-[(4-*O*-methyl-β-glucopyranosyl)-oxy]benzoic Acid*; **3**): White, amorphous powder. UV (MeOH): 288 (2.58), 243 (2.88). IR (KBr): 3411, 2925, 1697, 1604, 1515, 1274. $^1H$- and $^{13}C$-NMR: *Table 1*. ESI-MS (pos.): 367.1 ($[M+Na]^+$). ESI-MS (neg.): 709.4 ($[2M+Na-2\,H]^-$), 343.2 ($[M-H]^-$), 166.9 ($[M-C_7H_{13}O_5]^-$). HR-ESI-MS (pos.): 345.1196 ($[M+H]^+$, $C_{15}H_{21}O_9^+$; calc. 345.1186).

*5-Methoxycinnamic Acid 3-(4′-*O*-methyl-β-glucopyranoside)* (=*(2*E*)-3-{3-Methoxy-5-[(4-*O*-methyl-β-glucopyranosyl)oxy]phenyl}prop-2-enoic Acid*; **4**): White, amorphous powder. UV (MeOH): 308 (3.76), 281 (3.85), 225 (3.80), 216 (3.86). IR (KBr): 3378, 2929, 1695, 1635, 1598, 1513, 1259, 1099. $^1H$- and $^{13}C$-NMR: *Table 2*. ESI-MS (pos.): 393.1 ($[M+Na]^+$), 177.0 ($[M-C_7H_{13}O_6]^+$). ESI-MS (neg.):

739.5 ([2*M* – H]$^-$), 369.2 ([*M* – H]$^-$), 193.0 ([*M* – $C_7H_{13}O_5$]$^-$). HR-ESI-MS (pos.): 393.1191([*M* + Na]$^+$, $C_{17}H_{22}O_9Na^+$; calc. 393.1162).

*Naphthalene-1,8-diol 1,8-Bis(4′-*O*-methyl-β-glucopyranoside)* (= *Naphthalene-1,8-diyl Bis(4-*O*-methyl-β-glucopyranoside)*; **5**): Yellow, amorphous powder. UV (MeOH): 285 (3.62), 227 (4.40). IR (KBr): 3411, 2931, 1579, 1384, 1271, 1082. $^1$H- and $^{13}$C-NMR: *Table 2*. ESI-MS (pos.): 1047.3 ([2*M* + Na]$^+$), 535.3 ([*M* + Na]$^+$). ESI-MS (neg.): 1023.4 ([2*M* – H]$^-$), 557.2 ([*M* + COOH]$^-$), 511.1 ([*M* – H]$^-$), 335.0 ([*M* – $C_7H_{13}O_5$]$^-$). HR-ESI-MS (pos.): 535.1780 ([*M* + Na]$^+$, $C_{24}H_{32}O_{12}Na^+$; calc. 535.1791).

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