Three New Homologous 3-Alkyl-1,4-benzoquinones from the Fruiting Bodies of *Daldinia concentrica*

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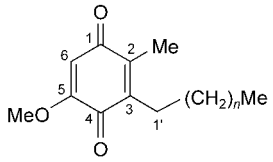
A new homologous series of 3-alkyl-5-methoxy-2-methyl-1,4-benzoquinones (**1**–**3**), with chain lengths of C_{21} to C_{23}, were isolated from the fruiting bodies of *Daldinia concentrica*, together with five known compounds. The molecular structures were established by spectroscopic methods.

Introduction. – Many unique secondary metabolites have been found in fungi of the ascomycete genus. More than four decades ago, *Allport* and *Bu'lock* studied European and American *Daldinia* sp. [1][2], which resulted in the identification of characteristic metabolites in their stromata and cultures. Some of those compounds had antimicrobial and nematocidal activities [3]. During the study of Japanese *Daldinia* sp., more than 20 new metabolites had been discovered [4–8], including cytochalasins, binaphthyl compounds, and some derivatives of azaphilone and benzophenone, some of which show a wide range of biological activities. As part of our ongoing studies [9–15] on the active metabolites from higher fungi in Yunnan province, China, we investigeted the chemical constituents of Chinese *Daldinia* species. Here, we report the structures of the three new 1,4-benzoquinones **1**–**3**, which were isolated from the $CHCl_3$ extract of the fruiting bodies of ascomycete *Daldinia concentrica*. The structures were elucidated by spectroscopic means.



1 n = 19
2 n = 20
3 n = 21

Results and Discussion. – The $CHCl_3$ extract of the fruiting bodies of *Daldinia concentrica* was subjected to repeated column chromatography (CC) to afford a yellow powder. Negative FAB-MS showed three molecular-ion peaks at m/z 446 (100), 460 (22) and 474 (27), differing by 14 mass units from each other, suggesting a mixture of three homologous compounds, which could not be separated from each other. On the basis of the HR-TOF-MS data, the following formulae were determined for the respective components: $C_{29}H_{50}O_3$ (**1**; 446.3759, M^-; calc. 446.3746), $C_{30}H_{52}O_3$ (**2**; 460.3916, M^-, calc. 460.3912), and $C_{31}H_{54}O_3$ (**3**; 474.4072, M^-, calc. 474.4060).

The quinoid nature of compounds **1**–**3** was evident from the UV (λ_{max} 275 nm) and IR ($\tilde{\nu}$ 1672, 1645, and 1605 cm^{-1}) spectral data, which are typical for 1,4-benzoquinones

[16]. The ^{1}H-NMR spectrum of **1**–**3** (see the *Table*) exhibited signals at δ(H) 0.85 (*t*, *Me*(CH$_2$)$_n$), 1.23 (*m*, Me(C*H*$_2$)$_n$CH$_2$), 2.01 (*s*, 2-Me), 2.46 (*t*, J = 7.3, Me(CH$_2$)$_n$C*H*$_2$), 3.76 (*s*, MeO), and 5.84 (*s*, H–C(6)). The ^{13}C-NMR spectrum gave rise to signals at δ(C) 187.7 (C=O), 182.0 (C=O), 158.4 (C$_q$), 143.2 (C$_q$), 141.2 (C$_q$), 107.1 (CH), 56.0 (Me), 14.1 (Me), 12.1 (Me), and 22.7–31.9 ((CH$_2$)$_n$). These data confirmed a MeO, a Me, and a long-chain alkyl group attached to a quinone nucleus. The locations of these groups were established by HMBC experminets (*Table*). Correlations were observed between δ(H) 2.01 (2-Me) and δ(C) 187.7 (C(1)); δ(H) 2.46, 5.84 (CH$_2$(1′), H–C(6)) and δ(C) 141.2 (C(2)); δ(H) 2.01 (2-Me) and δ(C) 143.2 (C(3)); δ(H) 2.46, 5.84 (CH$_2$(1′), H–C(6)) and δ(C) 182.0 (C(4)); and between δ(H) 3.76 (MeO) and δ(C) 158.4 (C(5)), corroborating that the benzoquinone H-atom at δ(H) 5.84 and the MeO group at δ(H) 3.76 were vicinal. Thus, the structures of **1**–**3** were assigned as 3-alkyl-5-methoxy-2-methyl-1, 4-benzoquinone, the n-alkyl group being C$_{21}$H$_{43}$, C$_{22}$H$_{45}$, and C$_{23}$H$_{47}$, respectively. Thus, the structures are 3-heneicosyl- (**1**) and 3-docosyl-5-methoxy-2-methyl-1,4-benzoquinone (**2**), and 5-methoxy-2-methyl-3-tricosyl-1,4-benzoquinone (**3**).

Table 1. *^{1}H- and ^{13}C-NMR Spectral Data of a Ternary Mixture of* **1**, **2**, *and* **3**. In CDCl$_3$; δ in ppm, J in Hz.

	δ(C)	δ(H)	HMBC (selected)
C(1)	187.7		2-Me
C(2)	141.2		H–C(6), CH$_2$(1′)
C(3)	143.2		Me(7)
C(4)	182.0		H–C(6), CH$_2$(1′)
C(5)	158.4		MeO
H–C(6)	107.1	5.84 (*s*)	
2-Me	12.1	2.01 (*s*)	
MeO	56.0	3.76 (*s*)	
CH$_2$(1′)	26.3	2.46 (*t*, J = 7.3)	
CH$_2$(2′) to CH$_2$(*n*′)[a]	31.9–22.7	1.23 (*m*)	
*Me*CH$_2$	14.1	0.85 (*t*, J = 6.4)	

[a]) n = 20 (**1**), 21 (**2**), or 22 (**3**).

Together with compounds **1**–**3**, the following known constituents were isolated from *D. concentrica:* friedelin [17], ergosta-4,6,8(14),22-tetraen-3-one [18], ergosta-7,22-dien-3-one [19], as well as (22*E*,24*R*)-ergosta-7,22-dien-3β-ol and ergosta-5,7,22-trien-3β-ol [18][20].

Experimental Part

General. Melting points (m.p.): *XRC-1* apparatus (Sichuan University, Sichuan, China). Optical rotations: *Horiba SEPA-300* automatic polarimeter (*Horiba*, Tokyo, Japan). IR Spectra: *Bruker Tensor-27* spectrophotometer (*Bruker*, Karlsruhe, Germany); KBr technique, in cm^{-1}. NMR Spectra: *Bruker DRX-500* NMR (*Bruker*, Karlsruhe, Germany); at 400 (^{1}H) and 100 MHz (^{13}C); δ in ppm rel. to SiMe$_4$ as internal standard, J in Hz. MS: *VG Autospec-3000* mass spectrometer (*VG*, Manchester, UK) and *API Qstar Pulsar* (*Applied Biosystems*, Foster City, USA); in *m*/*z*.

Fungal Material. Fruiting bodies of *Daldinia concentrica* were collected in Laojunshan, Yunnan, P. R. China, in 2003. A voucher specimen was deposited at the herbarium of the Kunming Institute of Botany, The Chinese Academy of Sciences.

Extraction and Isolation. Dried fruiting bodies (11.5 kg) of *D. concentrica* were extracted at r.t. with $CHCl_3$ (3×). The combined org. extracts were concnetrated *in vacuo* to afford a deep-brown gum (150 g), which was submitted to column chromatography (CC) (SiO_2; $CHCl_3$/MeOH). A total of 20 fractions were collected. The fractions eluted with $CHCl_3$/MeOH 100:1, 95:5, 9:1, and 8:2 afforded friedelin (6.3 mg), ergosta-4,6,8(14),22-tetraen-3-one (11.7 mg), and a binary mixture of (22*E*,24*R*)-ergosta-7,22-dien-3β-ol and ergosta-5,7,22-trien-3β-ol (36.9 mg), respectively, after recrystallization. The fraction eluted with $CHCl_3$/MeOH 9:1 (1.5 g) was subjected to CC (SiO_2; petroleum ether/acetone), yielding a ternary mixture of **1**, **2**, and **3** (11.2 mg), as well as ergosta-7,22-dien-3-one (27 mg).

Ternary Mixture of 3-Heneicosyl-5-methoxy-2-methyl-1,4-benzoquinone (**1**), *3-Docosyl-5-methoxy-2-methyl-1,4-benzoquinone* (**2**), *and 5-Methoxy-2-methyl-3-tricosyl-1,4-benzoquinone* (**3**). Yellow powder. UV ($CHCl_3$): 275 nm. IR (KBr): 3452, 2918, 2850, 1672, 1645, 1605, 1468, 1230, 1076, 721. ^{1}H- and ^{13}C-NMR: see the *Table*. FAB-MS (neg.): 446 (**1**; 100, M^-), 460 (**2**; 22, M^-), 474 (**3**; 27, M^-). HR-TOF-MS (neg.): 446.3746 (**1**; M^-, $C_{29}H_{50}O_3^-$; calc. 446.3760), 460.3912 (**2**; M^-, $C_{30}H_{52}O_3^-$; calc. 460.3916), 474.4060 (**3**; M^-, $C_{31}H_{54}O_3^-$; calc. 474.4073).

Friedelin. Colorless needles. M.p. 261–263° ($CHCl_3$). The MS and NMR data were consistent with those reported in [17].

Ergosta-4,6,8(14),22-tetraen-3-one. Pale yellow needles. M.p. 112–114° (petroleum ether/acetone). The MS and NMR data were consistent with those reported in [18].

Ergosta-7,22-dien-3-one. Colorless needles. M.p. 184–187° (petroleum ether/acetone). The MS and NMR data were consistent with those reported in [19].

*Binary Mixture of (22*E*,24*R*)-Ergosta-7,22-dien-3β-ol and Ergosta-5,7,22-trien-3β-ol.* Colorless needles. The MS and NMR data were consistent with those reported in [18][20].

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