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TWO NEW PHENOLIC COMPOUNDS FROM THE ANTARCTIC LICHEN *Pertusaria dactylina*

Man Hyung Goo,[1] Ji Hee Kim,[2] Hyun Park,[1,3] Jun Hyuck Lee,[1,3] and Ui Joung Youn[2,3*]

*Two new phenolic compounds, methyl 2-hydroxy-4-methoxy-6-(2-oxopentyl)-benzoate (**1**) and 4-methoxy-6-pentyl-1,2-dihydroxybenzene (**2**), together with two known phenolic derivatives, were isolated from the Antarctic lichen* Pertusaria dactylina *(*Pertusariaceae*). The structures of the new compounds were determined by 1D and 2D NMR and HR-MS experiments, as well as by comparison of their data with the published values.*

Keywords: *Pertusaria dactylina*, Antarctic lichen, Pertusariaceae, phenolic compounds.

The *Pertusaria* genus is distributed worldwide from the tropics to the Arctic and the Antarctic areas, which has about 800 species. There have been phytochemical reports on the diverse compounds, including xanthones [1], depsides [2], depsones [3], and fatty acids [4] from several species, such as Chinese *Pertusaria* sp., *P. amara*, *P. albescens*, *P. flavicans*, *P. pseudocorallina*, and *P. truncata.* Meanwhile, chemical and biological studies of *P. dactylina* collected from the Antarctic area have not been reported so far. In our continuous chemical research on the Antarctic lichen, two new monophenolic compounds, together with two known derivatives, have been isolated. This paper reports the isolation and structure elucidation of the new compounds.

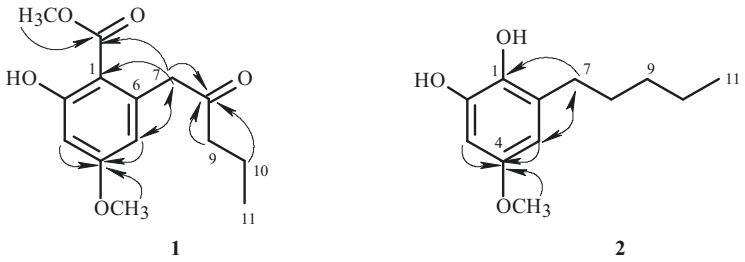
Compound **1** was obtained as a white amorphous powder, and the molecular formula $C_{14}H_{18}O_5$ was deduced from the positive-ion at *m/z* 266.1157 $[M]^+$ (calcd for $C_{14}H_{18}O_5$, 266.1154) in the HR-EI-MS spectrum. The NMR (Table 1) and HSQC spectra displayed signals for *meta*-coupled aromatic protons at δ_H 6.42 (d, J = 2.4 Hz)/δ_C 99.9 (C-3) and at δ_H 6.24 (d, J = 2.4 Hz)/δ_C 112.9 (C-5), two oxygenated aromatic carbons at δ 164.1 (C-2) and δ 165.7 (C-4), and two quaternary aromatic carbons at δ 138.8 (C-6) and δ 105.0 (C-1), indicative of a tert-substituted monophenyl group. The ^{1}H NMR spectrum showed two methoxy protons (δ 3.83, 3.82) and a hydroxy proton downfield shifted (δ 11.62) due to the hydrogen bonding with a carbonyl carbon (δ 170.8), which were confirmed from their position in the aromatic ring by the HMBC analysis (Fig. 1). In addition, two methylenes [δ_H 2.41 (t, J = 7.2 Hz)/δ_C 43.8 (C-9) and δ_H 1.61 (m)/δ_C 17.0 (C-10)] and a methyl group at δ_H 0.93 (t, J = 7.8 Hz)/δ_C 13.7 (C-11), indicating a propyl moiety, a downfield-shifted methylene at δ_H 3.90 (s)/δ_C 51.3 (C-7), and a ketonic carbon at δ 207.3 (C-8) were observed in the NMR and HSQC spectra. Compound **1** is quite similar to **3**, except for a ketonic carbon (C-8), and a downfield-shifted methelene group (C-7). The HMBC correlations of the methylene proton (H-7) with the ester carbonyl carbon at δ_C 170.8, C-5, and the ketonic carbon (C-8) and of H-9 with C-8 indicated the presence of 2-oxopropyl moiety compared to that of depsitrus B [5].

Thus, compound **1** was elucidated as a new compound, methyl 2-hydroxy-4-methoxy-6-(2-oxopentyl)-benzoate.

1) Unit of Polar Genomics, Korea Polar Research Institute, 21990, Incheon, Republic of Korea; 2) Division of Life Sciences, Korea Polar Research Institute, KIOST, 21990, Incheon, Republic of Korea, fax: +82 32 760 5509, e-mail: ujyoun@kopri.re.kr; 3) Department of Polar Sciences, University of Science and Technology, 21990, Incheon, 21990, South Korea. Published in *Khimiya Prirodnykh Soedinenii*, No. 1, January–February, 2020, pp. 29–30. Original article submitted December 20, 2018.

TABLE 1. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR Data for Compounds **1** and **2** ($CDCl_3$, δ, ppm, J/Hz)

C atom	**1**		**2**	
	δ_C	δ_H	δ_C	δ_H
1	105.0 (C)	–	141.4 (C)	–
2	164.1 (C)	–	157.9 (C)	–
3	99.9 (CH)	6.42 (d, J = 2.4)	97.5 (CH)	6.21 (d, J = 2.4)
4	165.7 (C)	–	158.1 (C)	–
5	112.9 (CH)	6.24 (d, J = 2.4)	108.4 (CH)	6.19 (d, J = 2.4)
6	138.8 (C)	–	124.0 (C)	–
7	51.3 (CH_2)	3.90 (s)	34.9 (CH_2)	2.56 (t, J = 8.7)
8	207.3 (C)	–	30.9 (CH_2)	1.62 (m)
9	43.8 (CH_2)	2.41 (t, J = 7.2)	32.1 (CH_2)	1.32 (m)
10	17.0 (CH_2)	1.61 (m)	23.7 (CH_2)	1.33 (m)
11	13.7 (CH_3)	0.93 (t, J = 7.8)	14.5 (CH_3)	0.89 (t, J = 7.2)
1-$\underline{CO}OCH_3$	170.8 (C)	–		
1-$COO\underline{CH_3}$	51.8 (C)	3.83 (s)		
4-OCH_3	55.4 (C)	3.82 (s)	55.9 (C)	3.72 (s)



1 **2**

Fig. 1. Key HMBC correlations of compounds **1** and **2**.

Compound **2** was obtained as a white amorphous powder, and the molecular formula $C_{12}H_{18}O_3$ was deduced from the positive-ion at *m/z* 210.1250 $[M]^+$ (calcd for $C_{12}H_{18}O_3$, 210.1256) in the HR-EI-MS spectrum. The ^{1}H NMR spectrum of **2** displayed a set of AB type aromatic protons at δ 6.21 and 6.19, which was similar to that of **1**. However, **2** showed only one methoxy signal and four methylene protons from δ 2.56 to 1.32 and a methyl proton at δ 0.89, indicating the presence of a pentyl group instead of 2-oxopentyl group in **1**. The ^{13}C NMR spectrum revealed three oxygenated aromatic carbons at δ 158.1 (C-4), 157.9 (C-2), and 141.4 (C-1), two protonated aromatic carbons at δ_C 108.4 (C-5) and 97.5 (C-3), a methoxy carbon at δ 55.9, four methylenes [δ 34.9 (C-7), 30.9 (C-8), 32.1 (C-9), and 23.7 (C-10)], and a methyl carbon at δ 14.5 (C-11), implying the absence of -$COOCH_3$ and a ketonic group in **1**. This observation was further supported by the HMBC correlations from the methoxy proton (4-OCH_3), H-3, and H-5 to C-4, and from H-7 to C-1, C-5, and C-6 (Fig. 1). Accordingly, compound **2** was elucidated as a new compound, 4-methoxy-6-pentyl-1,2-dihydroxybenzene.

The known compounds were identified as methyl 2-hydroxy-4-methoxy-6-pentylbenzoate (**3**) [6] and monomethyl olivetol (**4**) [7] by comparison of their physical and spectral properties with published values.

EXPERIMENTAL

General Methods. Optical rotations were measured on a Rudolph Research Autopol IV multiwavelength polarimeter. UV spectra were recorded on a Shimadzu PharmaSpec-1700 UV-visible spectrophotometer. IR spectra were measured on a Bruker Tensor-27 spectrophotometer. 1D and 2D NMR spectra were recorded on a Bruker Avance (600 MHz) spectrometer. High-resolution electrospray ionization mass spectra (HR-EI-MS) were obtained with an Agilent 6530 LC-QTOF High Mass Accuracy mass spectrometer operated in the positive- and negative-ion modes. Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} (0.25 mm, Merck, Germany). Silica gel (230–400 mesh, Merck, Germany) and RP-18 (YMC·GEL ODS-A, 12 nm, S-150 μm) were used for column chromatography. Semipreparative HPLC was conducted on a YL9100 HPLC system (Young Lin, South Korea) equipped with a UV/Vis detector using an Alltech reversed-phase YMC-Pak C-18 column (10 μm, 20 × 250 mm) with a flow rate of 2 mL/min.

Lichen Material. The lichen, *P. dactylina*, was collected in January 2017 from King George Island, Antarctica (62°12′53.69″S; 58°55′23.87″ W) and identified by Dr. Ji Hee Kim and Miss Jae Eun So. A voucher specimen (No. Ant-053) was deposited at the Natural Product Chemistry Laboratory of the Korea Polar Research Institute.

Extraction and Isolation. The air-dried and powdered lichen *P. dactylina* (80 g) was extracted by maceration in MeOH (3 × 0.5 L) at room temperature. The solvent was concentrated *in vacuo* to yield 3 g of a crude extract, which was then suspended in distilled water (0.15 L) and extracted successively with *n*-hexane (2 × 0.2 L), EtOAc (2 × 0.2 L), and *n*-butanol (2 × 0.2 L). The EtOAc partitions (1.5 g) were separated by column chromatography over a C_{18} gel column and eluted with MeOH–H_2O (10:90 to 100% MeOH) to obtain 10 subfractions (ER1 to ER10). Subfraction ER3 (40 mg) was subjected to a second round of chromatography with an open Sephadex LH-20 (50 g) gel column using solvent mixtures (MeOH–H_2O, 20:80 to 100% MeOH) and purified by HPLC on a semipreparative RP-18 gel column, using MeOH–H_2O mixtures, from 20:80 to 90:10, as the solvent system, to yield **1** (1.5 mg, t_R 75 min), **2** (0.5 mg, t_R 80 min), and **3** (7.0 mg, t_R 83 min). Subfraction ER6 (50 mg) was purified over a silica gel column using $CHCl_3$–MeOH mixtures (from 100:0 to 70:30) as the solvent system to yield seven subfractions (ER6S1 to ER6S7). The combined subfractions ER6S2 and ER6S3 (30 mg) were subjected to separation on a semipreparative RP-18 column by HPLC using MeOH–H_2O mixtures (from 30:70 to 90:10) as the solvent system to yield compound **4** (8 mg, t_R 85 min).

Methyl 2-Hydroxy-4-methoxy-6-(2-oxopentyl)-benzoate (1). White amorphous powder. UV (MeOH, λ_{max}, nm) (log ε): 260 (4.0). IR (KBr, ν_{max}, cm^{-1}): 3330, 1760. For ^1H (600 MHz) and ^{13}C NMR (150 MHz) data, see Table 1. HR-ESI-MS *m/z* 266.1157 $[M]^+$ (calcd for $C_{14}H_{18}O_5$, 266.1154).

4-Methoxy-6-pentyl-1,2-dihydroxybenzene (2). White amorphous powder. For ^1H (600 MHz) and ^{13}C NMR (150 MHz) data, see Table 1. HR-ESI-MS *m/z* 210.1250 $[M]^+$ (calcd for $C_{12}H_{18}O_3$, 210.1256).

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