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A NEW MONOAROMATIC COMPOUND FROM THE LICHEN *PARMOTREMA TSAVOENSE* (KROG & SWINSCOW) KROG & SWINSCOW (PARMELIACEAE)

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ABSTRACT

A new monoaromatic compound, methyl (E)-2,4-dihydroxy-6-methyl-3-(3-oxobut-1-en-1-yl)benzoate (1), together with two common lichen metabolites atranol (2), 2-O-methylatranol (3) were isolated from the lichen Parmotrema tsavoense (Krog & Swinscow) Krog & Swinscow. Their chemical structures were established by 1D NMR, 2D NMR, high resolution ESI–MS spectroscopic analysis and comparison with those reported in the literatures.

Keywords: atranol, lichen metabolites, monoaromatic compound, *Parmotrema tsavoense*.

TÓM TẮT

Một hợp chất đơn vòng mới từ loài địa y Parmotrema tsavoense (Krog & Swinscow) Krog & Swinscow (Parmeliaceae)

Một hợp chất đơn vòng mới, methyl (E)-2,4-dihydroxy-6-methyl-3-(3-oxobut-1-en-1-yl)benzoate (1), cùng với hai hợp chất địa y phổ biến khác, atranol (2), 2-O-methylatranol (3), đã được cô lập từ loài địa y Parmotrema tsavoense (Krog & Swinscow) Krog & Swincow. Cấu trúc hóa học của chúng được xác định bằng các phương pháp phổ nghiệm cũng như so sánh với các tài liệu tham khảo.

Từ khóa: atranol, hợp chất đơn vòng thơm, hợp chất từ địa y, *Parmotrema tsavoense*.

1. Introduction

Our previous phytochemical study on the lichen *Parmotrema tsavoense* (Duong 2015) led to the isolation of new phenolic compounds such as depsidones and diphenyl ethers.[3] Some monoaromatic compounds were also reported from this lichen and these metabolites possess various biological activities such as cytotoxicity, antibacterial activity according to Boustie & Grube (2007) [1], Boustie *et al.* (2010) [2], Muller (2001) [5].

In this paper, we reported the isolation of one new compound, methyl (*E*)-2,4-dihydroxy-6-methyl-3-(3-oxobut-1-en-1-yl)benzoate (1), together with two known ones, atranol (2), 2-*O*-methylatranol (3), from the lichen *Parmotrema tsavoense*. Their chemical structures were elucidated by spectroscopic data analysis and comparison with those reported in the literature.

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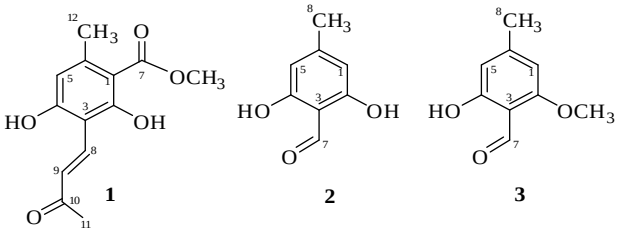

Figure 1. *Chemical structures of* ***1-3***

2. Experimental

General experimental procedures

The NMR spectra were measured on a Bruker Avance III (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) and Varian Mercury-400 Plus NMR (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometers with TMS as internal standard. Proton chemical shifts were referenced to the solvent residual signal of $CDCl_3$ at δ_H 7.26, of CD_3COCD_3 at δ_H 2.05, of DMSO-d_6 at δ_H 2.50. The ^{13}C–NMR spectra were referenced to the central peak of $CDCl_3$ at δ_C 77.1, of CD_3COCD_3 at δ_C 29.4, of DMSO-d_6 at δ_C 39.5. The HR–ESI–MS were recorded on a Bruker micrOTOF Q-II. TLC was carried out on precoated silica gel 60 F_{254} or silica gel 60 RP–18 $F_{254}S$ (Merck) and spots were visualized by spraying with 30% H_2SO_4 solution followed by heating. Gravity column chromatography was performed with silica gel 60 (0.040–0.063 mm, Himedia).

Figure 2. *Parmotrema tsavoense on rock*

Plant material

Parmotrema tsavoense (Krog & Swinscow) Krog & Swinscow was collected on the surface of rocks on Ta Cu mountain, Binh Thuan province (August-September 2012). Its scientific name was determined by Dr. Wetchasart Polyiam, Lichen Research Unit, Department of Biology, Faculty of Science, Ramkhamhaeng University, Bangkok, Thailand. A voucher specimen (No US-B027) was deposited in the herbarium of the Department of Organic Chemistry, University of Science.

Extraction and isolation

The clean, air-dried and ground material (1350 g) was extracted by methanol at ambient temperature, and the filtrated solution was concentrated under reduced pressure. While the methanolic solution was being evaporated, a precipitate (79.7 g) occurred and was filtered off. The rest of the solution was evaporated to dryness to obtain a crude methanol extract (249.8 g). This crude extract was applied to normal phase silica gel

column chromatography, eluted with the solvent system of *n*-hexane–ethyl acetate (9:1) to afford fraction **P1** (9.9 g). Consecutive elution of the column with the same solvent system but increasing polarity (8:2, 7:3, 6:4, 5:5, 4:6) yielded five fractions, **P2** (2.8 g), **P3** (3.3 g), **P4** (3.1 g), **P5** (16.1 g), and **P6** (9.9 g), respectively. Finally, the remaining residue was eluted with ethyl acetate–methanol in the ratios (9:1) and (0:10), respectively, to afford two fractions, **P7** (5.1 g) and **M** (80.1 g). A part of the extract **P1** (1.0 g) was applied to silica gel column chromatography, eluted with *n*-hexane–ethyl acetate–acetic acid (9:1:0.02) to give two compounds, **2** (10.7 mg) and **3** (3.4 mg).

The dry lichen material after macerating by methanol as described above was continuously macerated in acetone at ambient temperature to afford a crude acetone extract (42.1 g). This crude extract was applied to normal phase silica gel column chromatography, eluted with the solvent system of *n*-hexane–ethyl acetate–acetone–acetic acid (20:10:10:0.1) to afford five fractions **AC1**–**5**. Purifying fraction **AC1** (341.6 mg) by preparative TLC, eluted with *n*-hexane–chloroform–ethyl acetate–acetone–acetic acid (5:1:2:2:0.1) afforded compound **1** (3.2 mg).

- **Methyl (*E*)-2,4-dihydroxy-6-methyl-3-(3-oxobut-1-en-1-yl)benzoate (1)**: White amorphous powder. HR-ESI-MS *m/z* 249.0754 $[M-H]^-$ (calcd. for $C_{13}H_{13}O_5$–H, 249.0763). The ^{1}H- (500 MHz) and ^{13}C- NMR (125 MHz) data (Acetone-d_6): see Table 1. HMBC correlations: see Figure 3.
- **Atranol (2)**: White amorphous powder. The ^{1}H-NMR (400 MHz) data ($CDCl_3$): see Table 1. These spectroscopic data were suitable with with those reported in the literatures [4].

2-*O*-Methylatranol (3): White amorphous powder. The ^{1}H-NMR (400 MHz) data (DMSO-d_6): see Table 1. These spectroscopic data were suitable with those reported in the literature [4].

3. Results and discussion

Compound **1** was isolated as an amorphous powder. The molecular formula of **1** was determined to be $C_{13}H_{14}O_5$ using HRESIMS. The ^{1}H and ^{13}C spectra revealed the presence of one aromatic methine (δ_H 6.45, δ_C 111.6), two olefinic methine groups (δ_H 7.94, δ_C 133.5, C-8; δ_H 7.22, δ_C 129.3, C-9), two methyls (δ_H 2.48, δ_C 23.6, C-12; δ_H 2.40, δ_C 14.3, C-11), one methoxy group (δ_H 3.96, δ_C 51.8), two carbonyl groups (δ_C 172.2, 197.9), and five aromatic quaternary carbons. From these data, **1** was presumed to be an orcinol derivative containing a 3-oxobuta-2-enyl side chain at C-3. The large coupling constants of H-8 (δ_H 7.94, d, J = 16.5 Hz) and H-9 (δ_H 7.22, d, J = 16.5 Hz) proved that this alkene possessing a *trans* configuration. Proton H-8 shifted to the low field indicating the conjugated system of the double bond at C-8/C-9 and a methylketone group at C-10 (δ_C 197.9). This finding was supported by HMBC correlations of H-8, H-9, and CH_3-11 to C-10 (Figure 3).

In the HMBC spectrum, the correlations of H-5 to C-1 (δ_C 103.3), C-12 (δ_C 23.6), of CH_3-6 to C-1 (δ_C 103.3), C-5 (δ_C 111.6) deduced the adjacent positions of H-5, CH_3-6 and 1-CO_2CH_3 groups. Moreover, the proton H-8 showed the HMBC cross peaks to C-2 (δ_C 165.0), C-3 (δ_C 107.5), and C-4 (δ_C 161.0) and proton H-5 showed cross peaks to C-3 and C-4 indicated the attachment of the side chain at C-3. The assignment of the chelated hydroxyl group was determined at C-2 due to HMBC correlations of 2-OH to C-1 and C-2. Further HMBC correlations confirmed the chemical structure of **1**. Accordingly, **1** was elucidated as methyl (*E*)-2,4-dihydroxy-6-methyl-3-(3-oxobut-1-en-1-yl)benzoate.

Table 1. *^{1}H NMR data of **1–3***

	1[a] (Acetone-d_6)		**2**[b] ($CDCl_3$)	**3**[b] (DMSO-d_6)
	(*multi, J, Hz*)		(*multi, J, Hz*)	(*multi, J, Hz*)
N	δ_H	δ_H	δ_H	δ_H
1		6.20 (*br*)	6.20 (*br*)	6.15 (*br*)
2				
3		6.20 (*br*)	6.20 (*br*)	6.15(*br*)
4				
5	6.45 (*s*)			
6				
7		10.29 (*s*)	10.29 (*s*)	10.68 (*s*)
8	7.94 (*d, 16.5*)	2.26 (*br*)	2.26 (*br*)	2.27 (*s*)
9	7.22 (*d, 16.5*)			
10				
11	2.27 (*s*)			
12	2.48 (*s*)			
7-OCH_3	3.96 (*s*)			
2-OCH_3				3.79 (*s*)
2-OH	12.86 (*br*)			

[a] recorded in 500 MHz, [b] recorded in 400 MHz

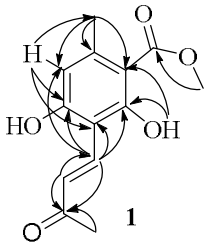

Figure 3. *HMBC correlations of **1***

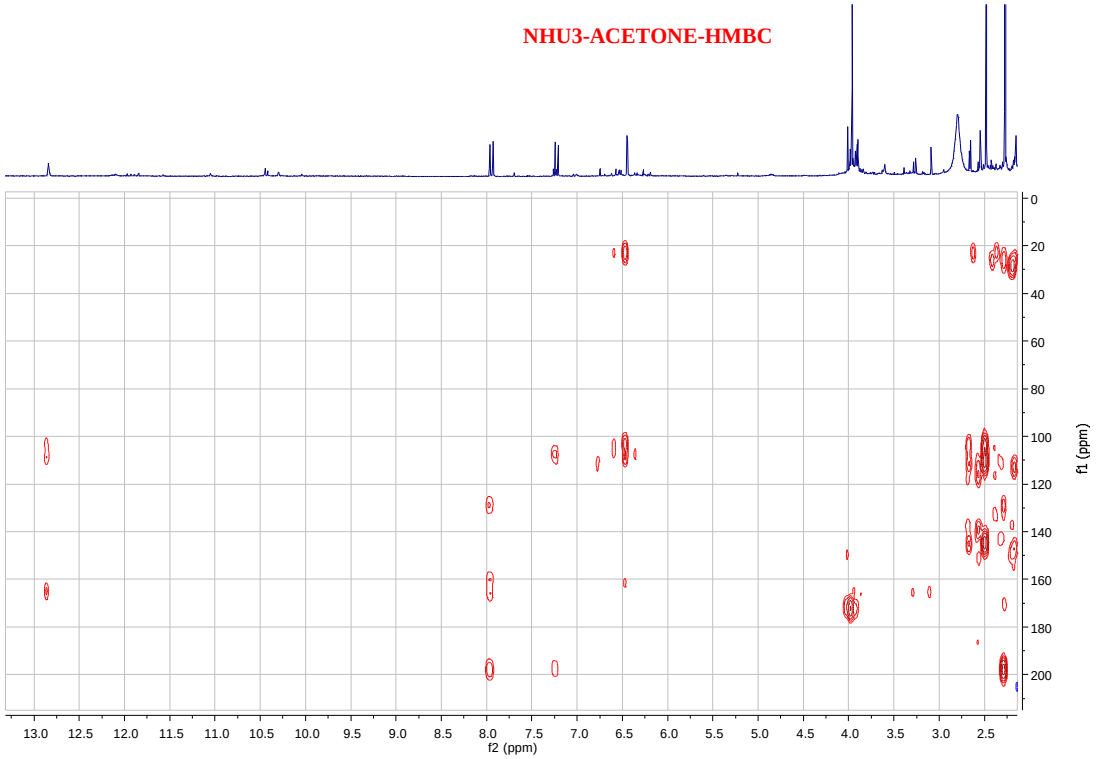

Figure 4. *HMBC spectrum of 1*

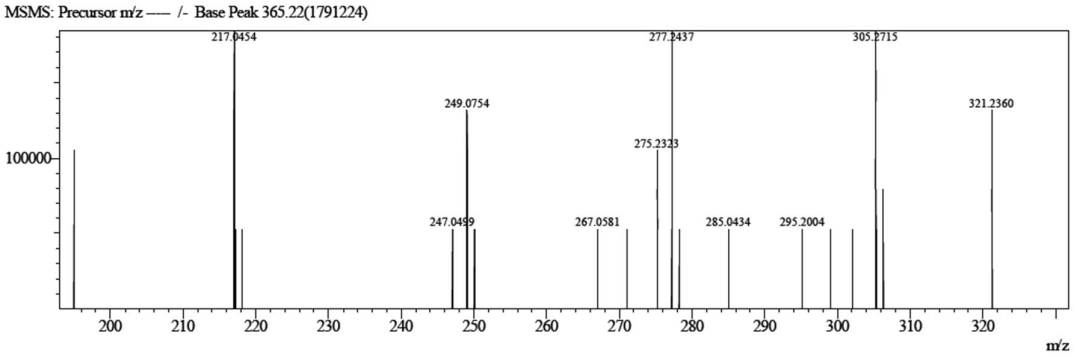

Figure 5. *HR-ESI-MS spectrum of* ***1***

4. Conclusion

A new compound methyl (*E*)-2,4-dihydroxy-6-methyl-3-(3-oxobut-1-en-1-yl)benzoate (**1**), together with two known ones, atranol (**2**) and 2-*O*-methylatranol (**3**), were isolated from the lichen *Parmotrema tsavoense* collected in Binh Thuan province. This is the first time the two compounds **2** and **3** were found in this lichen. Further studies on this lichen are in progress.

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