SOME PHENOLIC COMPOUNDS FROM LICHEN
PARMOTREMA SANCTI-ANGELII (LYNGE) HALE
(PARMELIACEAE)

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ABSTRACT

Four known phenolic compounds 5,7-dihydroxy-1(3H)-isobenzofuranone (1), methyl lecanorate (2), orcinol (3), and skyrin (4) were isolated from the lichen Parmotrema sancti-angelii (Lynge) Hale. Their chemical structures were established by 1D NMR, high resolution ESI-MS spectroscopic analysis and comparison with those reported in the literatures. This is the first time these compounds are reported in Parmotrema sancti-angelii (Lynge) Hale.

Keywords: Parmotrema sancti-angelii, depside, monocyclic compounds, skyrin

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TÓM TÁT

Một số hợp chất phenol từ loài địa y Parmotrema sancti-angelii (Lynge) Hale (Parmeliaceae)

Bốn hợp chất phenol 5,7-dihydroxy-1(3H)-isobenzofuranone (1), methyl lecanorate (2), orcinol (3) và skyrin (4) được cất lập từ loại địa y Parmotrema sancti-angelii (Lynge) Hale. Cấu trúc hóa học của chúng được xác định bằng các phương pháp phổ phổ nhiệm cũng như so sánh với các tài liệu tham khảo. Đây là lần đầu tiên các hợp chất này được tìm thấy trong loại địa y Parmotrema sancti-angelii (Lynge) Hale.

Từ khóa: Parmotrema sancti-angelii, depside, monocyclic compounds, skyrin.

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1. Introduction

Phenolic compounds from lichen are bioactive compounds with various activities according to Boustie & Grube (2007), Boustie et al. (2010), Muller (2001). Seven phenolic compounds alectoronic acid, atranorin, α-collactolic acid, furmaprotocetraric acid, hypoprotocetraric acid, protocetraric acid, and lecanoric acid, demonstrating bactericidal activity from Parmotrema sancti-angelii were reported by Verma et al. (2011). They possessed the common skeletons as depsidone, depside, and diphenyl ether.

In this paper, from the lichen Parmotrema sancti-angelii collected in Lam Dong province, four known phenolic compounds 5,7-dihydroxy-1(3H)-isobenzofuranone (1), methyl lecanorate (2), orcinol (3), and skyrin (4) were isolated by using efficient separation techniques. Their chemical structures were elucidated by spectroscopic data analysis and comparison with those reported in the literature.

2. Experimental

General experimental procedures

The NMR spectra were measured on a Bruker Avance III (500 MHz for 1H NMR and 125 MHz for 13C NMR) spectrometers with TMS as internal standard. Proton chemical shifts were referenced to the solvent residual signal of CDCl3 at δH 7.26, of CD3COCD3 at δH 2.05, of CD3OD at δH 3.31. The 13C–NMR spectra were referenced to the central peak of CDCl3 at δC 77.1, of CD3COCD3 at δC 29.4, of CD3OD at δC 49.0. The HR–ESI–MS were recorded on a Bruker microTOF Q-II. TLC was carried out on precoated silica gel 60 F254 or silica gel 60 RP–18 F254S (Merck) and spots were visualized by spraying with 30% H2SO4 solution followed by heating. Gravity column chromatography was performed with Silica gel 60 (0.040–0.063 mm, Himedia).

Plant material

Parmotrema sancti-angelii (Lynge) Hale was collected on the bark of tea trees Camellia sinensis at Bao Loc city, Lam Dong province, Vietnam (07/2013–09/2013) and the scientific name was identified by Dr. Harrie J. M. Sipman, Botanic Garden and Botany Museum Berlin-Dahlem, Freie University, Berlin, Germany. A voucher
specimen (No US-B021) was deposited in the herbarium of the Department of Organic Chemistry, University of Science, Vietnam National University - Ho Chi Minh City, Vietnam.

**Extraction and isolation**

The clean, air-dried and ground material (950 g) was extracted by maceration with acetone at ambient temperature, and the filtrated solution was evaporated under reduced pressure to afford the crude acetone extract (145.1 g). The crude acetone extract (145.1 g) was dissolved in hot acetone (45 °C) to obtain two parts, the solution and the insoluble powder (P, 30.0 g). The solution was evaporated to afford the acetone extract (110.4 g). This one was applied on normal phase silica gel column chromatography, eluted with the solvent system of hexane–ethyl acetate (9:1) to afford H0 extract (6.1 g). Continuous elution of the column with the same solvent systems but increasing polarity (8:2), (7:3), (6:4), (4:6), and (3:7) yielded five fractions, H1 (2.1 g), C (15.4 g), EA1 (4.5 g), EA2 (5.1 g), and EA3 (9.8 g), respectively.

Extract EA1 (4.5 g) was applied to silica gel column chromatography, eluted with hexane–ethyl acetate–acetone (9:1:0.5) to give four fractions, EA1.1 (1.9 g) and EA1.2–1.4 (2.1 g). Fraction EA1.1 (1.9 g) was fractionated by column chromatography, eluting with hexane–ethyl acetate–acetic acid (9:1:0.5) to give two fractions, EA1.1.1 (998.9 g) and EA1.1.2 (219.5 mg). Fraction EA1.1.1 was further chromatographed, eluted with hexane–ethyl acetate–acetone (9:1:0.5) to afford 1 (395.7 mg) and 2 (4.9 mg). Fraction EA1.1.2 (219.5 mg) was purified, eluting with hexane–ethyl acetate–methanol (7:3:0.02) to obtain 3 (14.7 mg) and 4 (3.8 mg).

- **5,7-Dihydroxy-1(3H)-isobenzofuranone (1):** White amorphous powder. The 1H-NMR data (Acetone-\(d_6\)): 6.38 (1H, brs, H-3), 6.53 (1H, brs, H-5), 5.22 (2H, s, H-8). The 13C-NMR data (Acetone-\(d_6\)): 104.4 (C-1), 166.2 (C-2), 102.0 (C-3), 158.8 (C-4), 103.1 (C-5), 151.5 (C-6), 171.5 (C-7), 70.3 (C-8). These spectroscopic data were suitable with those reported in the literature.10

- **Methyl lecanorate (2):** White amorphous powder. The 1H-NMR data (CDCl₃): 6.30 (1H, d, J=2.0 Hz, H-3), 6.32 (1H, d, J=2.0 Hz, H-5), 2.61 (3H, s, H-8), 6.59 (1H, d, J=2.0 Hz, H-3’), 6.71 (1H, d, J=2.0 Hz, H-5’), 2.57 (3H, s, H-8’), 3.98 (-COOCH₃), 11.56 (s, 2-\(\text{OH}\)), 11.28 (s, 2’-\(\text{OH}\)). The 13C-NMR data (CDCl₃): 110.5 (C-1), 166.6 (C-2), 101.4 (C-3), 164.2 (C-4), 108.9 (C-5), 144.2 (C-6), 172.2 (C-7), 24.6 (C-8), 101.3 (C-1’), 161.0 (C-2’), 112.3 (C-3’), 154.2 (C-4’), 116.5 (C-5’), 143.6 (C-6’), 169.5 (C-7’), 24.9 (C-8’), 52.4 (-OCH₃). These spectroscopic data were suitable with those reported in the literatures.8
• **Orcinol (3):** White amorphous powder. The $^1$H-NMR data (CDCl$_3$): 6.23 (2H, d, J=1.5 Hz, H-1 & H-5), 6.16 (1H, brs, H-3), 2.24 (3H, s, H-7). These spectroscopic data were suitable with those reported in the literature.$^6$

• **Skyrin (4):** Red amorphous powder. HR-ESI-MS $m/z$ 537.0813 [M-H]- (calcd. for C$_{30}$H$_{17}$O$_{10}$, 537.0822). The $^1$H-NMR data (CDCl$_3$): 7.05 (2H, d, J=2.0 Hz, H-2 & H-2'), 7.35 (2H, J=1.5 Hz, H-4 & H-4'), 6.90 (2H,s, H-7 & H-7'), 2.34 (6H, s, 3-CH$_3$ & 3'-CH$_3$), 11.96 (s, 8-OH & 8'-OH), 12.84 (s, 1-OH & 1'-OH). The $^{13}$C-NMR data (Acetone-$d_6$): 163.0 (C-1 & C-1'), 124.4 (C-2 & C-2'), 149.2 (C-3 & C-3'), 121.1 (C-4 & C-4'), 123.6 (C-5 & C-5'), 165.2 (C-6 & C-6'), 108.4 (C-7 & C-7'), 166.1 (C-8 & C-8'), 191.5 (C-9 & C-9'), 183.2 (C-10 & C-10'), 132.8 (C-11 & C-11'), 110.9 (C-12 & C-12'), 114.0 (C-13 & C-13'), 134.7 (C-14 & C-14'), 21.9 (3-CH$_3$ & 3'-CH$_3$). These spectroscopic data were suitable with those reported in the literature.$^{3,5}$

3. **Results and discussion**

Compound 1 was obtained as a white amorphous powder. The $^1$H-NMR spectrum exhibited signals for one oxymethylene group at 5.22 (2H, s, H$_2$-8), two aromatic methine protons at $\delta_H$ 6.38 (1H, brs) and 6.53 (1H, brs). The chemical shift of H$_2$-8 shifted to low field indicated that this methylene group linked to a phenyl group and an ester group. The structure of 1 was confirmed by the $^{13}$C NMR data. The spectral data were suitable to the published ones.$^{10}$ Therefore, 1 was 5,7-dihydroxy-1(3H)-isobenzofuranone.

Compound 2 was obtained as a white amorphous powder. The $^1$H-NMR showed two singlets at $\delta_H$ 2.57 (3H) and 2.61 (3H) for methyl groups, a pair of doublets for two aromatic protons at $\delta_H$ 6.30 and 6.32 (each 1H, J=2.0Hz) for proton H-5 and H-3 and a pair of doublets at $\delta_H$ 6.59 and 6.71 (each 1H, J=2.0Hz) for proton H-5' and H-3', respectively. The $^{13}$C-NMR showed 16 carbon signals including two carboxyl groups (COO), four methine carbons, two methyls and eight aromatic substituted carbons. Comparison of the spectroscopic NMR data of 2 with those of methyl lecanorate$^8$ suggested that they were similar. Accordingly, 2 was elucidated as methyl lecanorate.

Compound 3 was obtained as a white amorphous powder. The $^1$H-NMR (CDCl$_3$) spectrum displayed signals of one methyl group at $\delta$ 2.24 (3H, s), three methine protons at $\delta$ 6.23 (2H, $d$, $J$ = 1.7 Hz, H-4 and H-6), 6.16 (1H, $t$, $J$ = 1.7 Hz, H-2). Analysis of the $^1$H-$^1$H spin-spin interaction of three aromatic protons revealed that 3 contained 1,3,5-trisubstituted benzene ring. These spectroscopic data were suitable to the published data,$^6$ therefore 3 was determined as orcinol.
Compound 4 was obtained as red amorphous powder. The $^1$H-NMR spectrum showed one methyl group $\delta_H$ 2.34, a pair of doublets for two aromatic protons at $\delta_H$ 7.05 and 7.35 (each 1H, J=2.0Hz), a singlet aromatic proton at $\delta_H$ 6.90, and two chelated hydroxyl groups at $\delta_H$ 11.96 and 12.84. These findings suggested that 4 possessed an anthraquinone skeleton. The $^{13}$C-NMR spectrum showed the signals of 14 carbons corresponding to one methyl, three aromatic methines, and ten quaternary carbons including three oxygenated and two carbonyl carbons. However, the HR-ESIMS established the molecular formula of 4 to be C$_{30}$H$_{18}$O$_{10}$, indicating a symmetrical structure. Accordingly, 4 was established as a bianthraquinone skyrin.$^{3,5}$

4. Conclusion

Four known phenolic compounds were also isolated from the lichen Parmotrema sancti-angelii collected in Lam Dong province. This is the first time these compounds are reported in Parmotrema sancti-angelii (Lynge) Hale. Further studies on this lichen are in progress.

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