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NOTE

A Novel β-Orcinol Depsidone of Lichen *Lobaria pulmonaria*

B. PEJIN[1,2,*], C. IODICE[2], B. STANIMIROVIC[3], V. VAJS[4] and V. TESEVIC[5]

[1]University of Belgrade, Institute for Multidisciplinary Research-IMSI, Department of Life Sciences, Kneza Viseslava 1, 11030 Belgrade, Serbia
[2]National Research Council of Italy-Institute of Biomolecular Chemistry, CNR-ICB, *via* Campi Flegrei 34, 80078 Pozzuoli (Naples), Italy
[3]Institute MOL Ltd, Nikole Tesle 15, 22300 Stara Pazova, Serbia
[4]University of Belgrade, Institute for Chemistry, Technology and Metallurgy-ICTM, Centre of Chemistry, Njegoseva 12, 11167 Belgrade, Serbia
[5]University of Belgrade, Faculty of Chemistry, Department of Organic Chemistry, Studentski trg 16, 11158 Belgrade, Serbia

*Corresponding author: E-mail: brspjn@gmail.com, boris.pejin@imsi.rs

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In continuation of our phytochemical survey of *Lobaria pulmonaria* has led to the identification of deoxystictic acid in this foliose lichen species for the first time. The isolated β-orcinol depsidone showed moderate anti-hydroxyl radical activity using fluorescence spectroscopy at *in vitro* conditions.

Keywords: Phytochemistry, Aromatic secondary metabolite, Anti-hydroxyl radical activity.

The majority of depsides, depsidones, dibenzofurans, usnic acids and depsones (secondary metabolites present in lichens) are formed by the bonding of two or three orcinol or β-orcinol-type phenolic units through ester, ether and carbon-carbon linkages. In addition to the ester linkage of the depsides, depsidones have an ether linkage resulting in a rigid polycyclic system[1]. The chemical composition of the lichen *Lobaria pulmonaria* was studied by Culberson[2] and González *et al.*[3] when reviewing *Lobaria* species, referred to it as having interesting combinations of β-orcinol depsidones. In continuation of our ongoing phytochemical investigation of *L. pulmonaria*[4,5] has led to the isolation of deoxystictic acid, a β-orcinol depsidone molecule with moderate anti-hydroxyl radical potential.

The lichen *Lobaria pulmonaria* (L.) Hoffm. (Lobariaceae) was collected from *Fagus sylvatica* on the mountain Zelengora (Bosnia and Herzegovina) in July 2009. Voucher specimen has been deposited in the Herbarium of the Institute of Botany, University of Belgrade, Serbia (BEOU 5997).

^{1}H NMR and ^{13}C NMR spectra were recorded at the NMR Service of the Institute of Biomolecular Chemistry of the National Research Council of Italy (CNR-ICB) on a Bruker Avance-400 spectrometer operating 400 and 100 MHz, respectively, using an inverse probe fitted with a gradient along the Z-axis, in $CDCl_3$, using the solvent signal as an internal standard. Thin-layer chromatography was carried out on pre-coated silica gel 60 F254 (0.25 mm, Merck, Darmstadt, Germany). LRMS and HRMS were recorded on a JEOL JMS D-300 and an AEI MS-50, respectively.

Before extraction the lichen was carefully inspected for contaminants. Air-dried parts of *L. pulmonaria* (70 g) were ground and extracted three times with $CHCl_3$, $CHCl_3$-MeOH 1:1, MeOH and MeOH-H_2O 1:1, respectively, (500 mL each) at room temperature, for up to 1 day each, with the extractives pooled and then evaporated *in vacuo*. The dried $CHCl_3$-MeOH (1:1) extract (5.81 g) was dissolved in H_2O (50 mL) and partioned sequentially with $CHCl_3$ (3 × 50 mL) and *n*-BuOH (3 × 50 mL). The crude insoluble coloured residue (0.46 g), obtained after the partition, was classified as fraction rich in epsilons, by means of its spectroscopic data and typical chromatographic profile. In order to further characterize the residue, it was chromatographed on Sephadex LH-20 column (20 mg) and eluted with the system of CH_2Cl_2-MeOH 1:1 to yield deoxystictic acid (1 mg, 0.0014 % of dry weight).

High-resolution mass spectrometry established the molecular formula of known depsidone deoxystictic acid ($C_{19}H_{14}O_8$, Fig. 1) which structure followed from 1-D and 2-D NMR spectra.

Deoxystictic acid (Fig. 1): ^{1}H NMR ($CDCl_3$-d_3, 400 MHz) δ 10.44 (1H, s, H-9), 6.72 (1H, s, H-5), 5.41 (2H, s, H-8'), 3.92 (3H, s, 0CH_3-4), 2.52 (3H, s, H-8), 2.23 (3H, s, H-9'); ^{13}C NMR ($CDCl_3$-d_3, 100 MHz) δ 186.9 (CHO, C-9), 171.2 (COO, C-7'), 163.1 (C, C-4), 161.1 (C, C-2), 151.8 (C, C-2'), 151.2 (C, C-6), 148.2 (C, C-4'), 136.9 (C, C-6'), 133.8 (C, C-5'),

1117.1 (C, C-3'), 113.2 (C, C-3), 106.2 (C, C-1'), 114.1 (C, C-1), 111.4 (CH, C-5), 69.8 (C, C-8'), 56.3 (C, 0CH_3-4), 21.9 (CH_3, C-8), 8.7 (CH_3, C-9'). ESIMS *m/z* 371.0733 $[M + H]^+$ (calcd. for $C_{19}H_{15}O_8$, 371.0766).

The spectral data presented are in good agreement with previously reported for the same compound isolated from the lichen *Hypotrachyna revoluta*[6]. According to the best of our knowledge, this is the first record of deoxystictic acid in *L. pulmonaria*. The isolated β-orcinol depsidone showed moderate anti-hydroxyl radical activity (68 ± 5 %) using fluorescence spectroscopy at *in vitro* conditions[7,8]. Further studies of β-orcinol depsidones of this species are in progress in our labs.

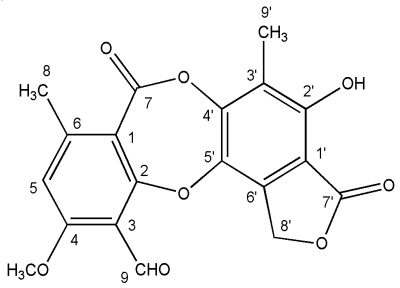

Fig. 1. Deoxystictic acid

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