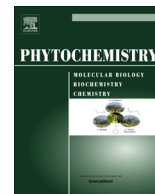




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Highly oxygenated chromones from mangrove-derived endophytic fungus *Rhytidhysterium rufulum*

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ABSTRACT

Five highly oxygenated chromones, rhytidchromones A–E, were isolated from the culture broth of a mangrove-derived endophytic fungus, *Rhytidhysterium rufulum*, isolated from Thai *Bruguiera gymnorhiza*. Their structures were determined by analysis of 1D and 2D NMR spectroscopic data. The structure of rhytidchromone A was further confirmed by single-crystal X-ray diffraction analysis. These compounds were evaluated for cytotoxicity against four cancer cell lines (MCF-7, Hep-G2, Kato-3 and CaSki). All compounds, except for rhytidchromone D, displayed cytotoxicity against Kato-3 cell lines with IC₅₀ values ranging from 16.0 to 23.3 μM, while rhytidchromones A and C were active against MCF-7 cells with IC₅₀ values of 19.3 and 17.7 μM, respectively.

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1. Introduction

Endophytic fungi, microorganisms which reside in the healthy tissue of their host harmoniously without causing any apparent negative effect (Strobel and Daisy, 2003; Faeth, 2002), are known as an exceptionally valuable resource for the discovery of structurally interesting and biologically active secondary metabolites, some of which are promising candidates for drug development or agrochemical applications (Zhang et al., 2006; Tan and Zou, 2001; Kusari and Spiteller, 2011; Strobel et al., 2004). Currently, an increasing number of fungal endophytes have been isolated and their metabolites are receiving considerable attention, with a number of structurally unique and biologically active compounds having been thus obtained from their cultures (Kharwar et al., 2011; Macías-Rubalcava et al., 2014; Liu et al., 2015; Amrani et al., 2014; Li et al., 2011). Among plant-derived fungi, those associated with a marine habitat, including mangrove plants, have received much interest from natural product researchers due to this ecosystem (Debbab et al., 2013; Xu, 2015; Zhou et al., 2014; Xiao et al., 2013). Moreover, Thailand has some of the largest mangrove formations in the world, with only those found in Bangla-

desh, Brazil, Indonesia and India being larger. This prompted us to embark on the study of bioactive metabolites from Thai mangrove-derived fungi (Pudhom and Teerawatananon, 2014; Pudhom et al., 2014; Chokpaiboon et al., 2011, 2010).

Recently, a chemical investigation of the endophytic fungal strain BG2-Y was performed. This fungus was isolated from the leaves of the Thai mangrove plant *Bruguiera gymnorhiza* and was identified as *Rhytidhysterium rufulum*. Five new chromones, namely rhytidchromones A–E (1–5), were obtained from the ethyl acetate (EtOAc) extract of the culture broth grown in a Sabouraud dextrose broth (SDB). These compounds contained a highly oxygenated side-chain in their structures. Herein, the isolation, structure elucidation, and cytotoxic activity against human cancer cell lines of these metabolites are described.

2. Results and discussion

The EtOAc extract of the mangrove-derived endophytic *R. rufulum* cultured in SDB was subjected to chromatographic fractionation over Sephadex LH20 and silica gel to yield compounds 1–5 (Fig. 1).

Rhytidchromone A (1), obtained as colorless crystals, was assigned a molecular formula of C₁₆H₁₆O₇ by the HRESIMS ion at *m/z* 343.0784 [M+Na]⁺, implying nine degrees of unsaturation. The ¹H NMR spectrum (Table 1) contained signals for one phenolic

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