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Phytochemical profile of *Schiekia orinocensis* (Haemodoraceae)

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ABSTRACT

Phytochemical investigation of different plant parts of *Schiekia orinocensis*, a neotropical member of the Haemodoraceae, resulted in the structure elucidation of thirteen phenylphenalenone-type compounds, five known flavonoids and one new 1,3-disubstituted glycerol derivative. Six of the phenylphenalenones are reported for the first time, among them five minor compounds derived from the reaction with acetone used for extraction. The occurrence of the phenylphenalenones possessing C_{19}, $C_{18}O$ or $C_{18}N$ skeletons confirmed the chemotaxonomic relationship of *S. orinocensis* with other members of the Haemodoraceae, especially the Haemodoroideae subfamily. The tissue-specific occurrence of the identified compounds was also subject to this study.

1. Introduction

The Haemodoraceae are known for the production of phenylphenalenones (Cooke and Edwards, 1981). The first compound of that type was isolated from *Haemodorum corymbosum* Vahl (Cooke and Segal, 1955). Later, phenylphenalenones and related compounds were also found in other monocotyledonous families such as Musaceae, Pontederiaceae and Strelitziaceae (DellaGreca et al., 2008; Hölscher and Schneider, 2000, 2005; Luis et al., 1994). In *Musa* species, these molecules, which are reported to be phytoalexins, are involved in the defense against phytopathogeneous fungi such as *Mycosphaerella fijensis* (Hidalgo et al., 2016) and the burrowing nematode *Radopholus similis* (Hölscher et al., 2014). The phenalenone-type compounds are inducible in the Musaceae, while constitutive and inducible phenylphenalenones may co-exist in the Haemodoraceae (Otálvaro et al., 2010). In continuation of our research on phenylphenalenones in the Haemodoraceae, this work investigates the phytochemical profile of *Schiekia orinocensis* (Kunth) Meisn., a species native to South America and found in mountain savannas and woodlands (Aerne-Hains and Simpson, 2017; Maas and Maas-van de Kamer, 2015; Simpson, 1998). In this work, the metabolic profile of different tissues of *S. orinocensis* has been investigated using LC–PDA–SPE–NMR and LC–MS analyses. In the Haemodoraceae, phenylphenalenones accumulate mainly in roots (Hölscher and Schneider, 1997) but have also been found both in vegetative above-ground plant parts (Fang et al., 2012b; Opitz and Schneider, 2002) and in generative organs (Chen et al., 2016). One of the aims of this work is therefore to study the tissue-specific occurrence of phenylphenalenones and other specialized metabolites in different parts of the *S. orinocensis* plant.

2. Results and discussion

2.1. Structure elucidation

Schiekia orinocensis plants were collected from a habitat located at the municipality of São Felix do Tocantins, at Tocantins state, Brazil. Rhizomes, stems, leaves, flowers and fruits were separately extracted, and the extracts chromatographically separated. The metabolites were analyzed by liquid chromatography–mass spectrometry (LC–MS) and liquid chromatography–photodiode array detection–solid phase extraction–nuclear magnetic resonance spectroscopy (LC–PDA–SPE–NMR) (Fig. 1A).

In total, 19 compounds (Fig. 1B) were identified from the *S. orinocensis* plant material. Among them, 13 compounds (**2**, **7-11**, **13-19**) could be classified as phenylphenalenones and related structures. Methoxyanigorufone (**19**) (Cooke and Thomas, 1975; Hölscher and Schneider, 1997) is the only phenylphenalenone in this plant possessing an unmodified C_{19} skeleton. 3,6-Dihydroxy-5-methoxy-7-phenyl-3*H*-benzo[*de*]isochrome-1-one (**15**) (Opitz et al., 2002), haemodordiol (**16**) (Brkljača and Urban, 2015), 6-hydroxy-3,5-dimethoxy-7-phenyl-3*H*-benzo[*de*]isochromen-1-one (**17**) (Fang et al., 2012b), and 4-hydroxy-3-methoxy-5-phenyl-1,8-naphthalic anhydride (**18**) (Cooke, 1970; Opitz

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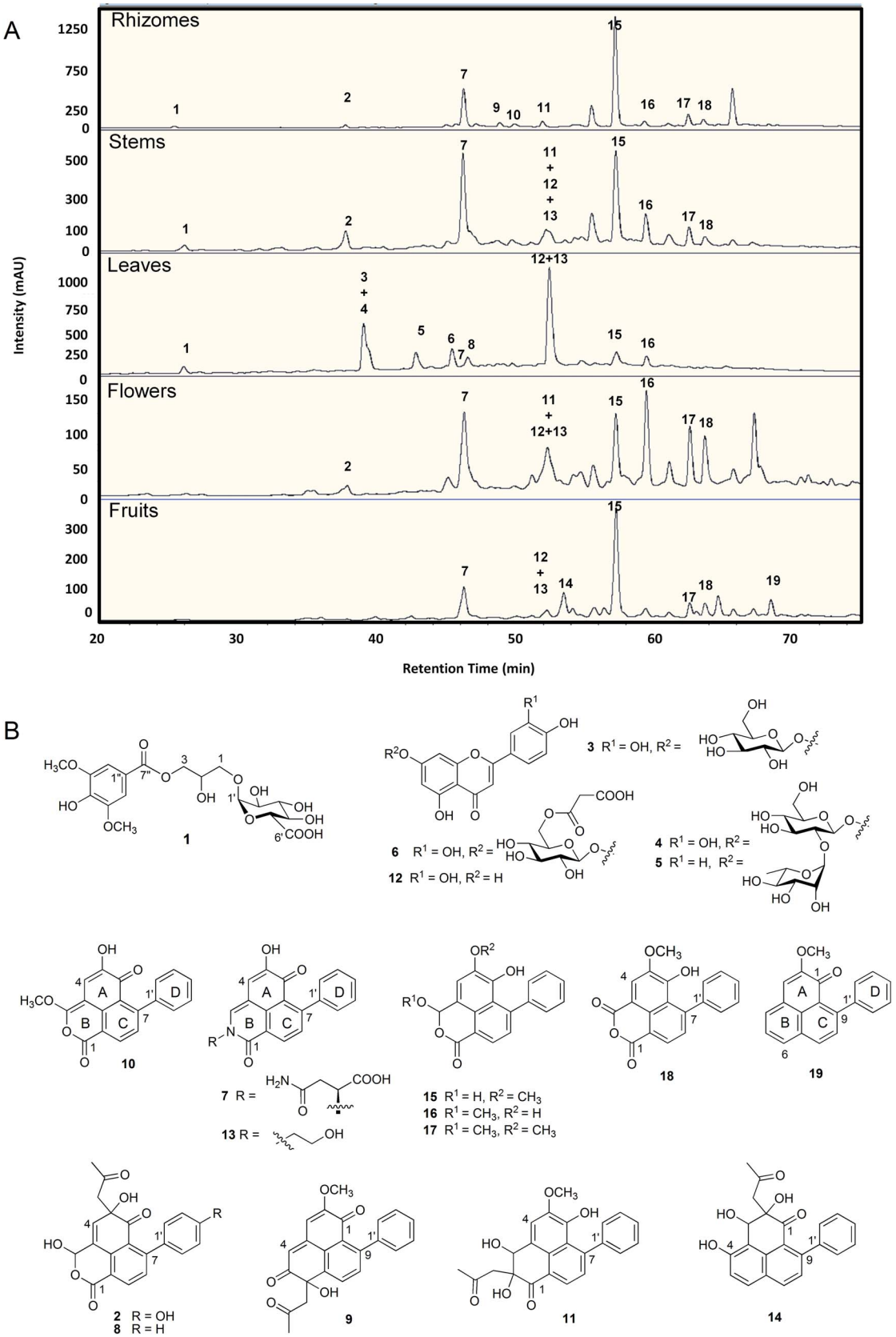

Fig 1. A) HPLC profile (λ= 254 nm) of different tissue extracts of *Schiekia orinocensis*. B) Structures of compounds isolated from *S. orinocensis*. Compounds **1** and **10**, and the acetonyl derivatives **2**, **8**, **9**, **11** and **14**, are reported here for the first time.

et al., 2002) are characterized by an oxidized phenylphenalenone skeleton ($C_{18}O$) and therefore named oxa-phenylphenalenones (Edwards and Weiss, 1972; Fang et al., 2012b). Oxa-phenylphenalenones can be considered as chemotaxonomic markers of the Haemodoroideae subfamily, because they are not found in Conostylidoideae, the other subfamily of the Haemodoraceae. All known compounds were