



Rapid isolation and identification of minor natural products by LC–MS, LC–SPE–NMR and ECD: Isoflavanones, biflavanones and bisdihydrocoumarins from *Ormocarpum kirkii*

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ABSTRACT

The combination of the hyphenated techniques LC–MS and LC–SPE–NMR constitutes a powerful platform for the rapid isolation and identification of minor components from natural sources. Electronic circular dichroism (ECD) is a useful tool to determine the absolute configuration of small quantities of chiral molecules. In order to search for minor constituents present in an *Ormocarpum kirkii* extract, these techniques were applied for the separation and structure elucidation of a series of isoflavanones, biflavanones and biscoumarins. After optimization of chromatographic conditions and subsequent isolation, MS and 1D and 2D NMR data were collected. Experimental and calculated ECD spectra were used in conjunction with NMR data to confirm the absolute configuration of these compounds. Eight compounds were identified for the first time and six have been previously reported. The present approach offers a strategy for accelerating research on natural products.

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1. Introduction

For the discovery of biologically active natural products, efficient use of time and resources is essential for reaching targeted outcomes. The standard procedure of searching for new natural products is biological screening and bioassay-guided fractionation. However, this process can be rather time-consuming and laborious. Based on *in vitro* screens, active compounds can easily be overlooked. In addition, there is a high chance of obtaining known and/or nuisance compounds, and the time and effort needed to isolate and to purify a known compound is the same as for a new one. Various attempts have been made to identify at an early stage of the isolation and purification procedure as many compounds as possible in a given mixture. Hyphenation of HPLC with NMR spectroscopy has emerged as an attractive approach for fast and reliable characterization of natural products from crude plant extracts. This approach has been used for identification of known compounds as well as for rigorous structure

elucidation of new compounds, i.e., sesquiterpene lactones, quinic acid derivatives, diterpenes, caffeoyl glycosides, and flavonoid glycosides (Jaroszewski, 2005a, 2005b). In addition, experimental and theoretically calculated electronic circular dichroism (ECD) spectra can be used to non-destructively determine the absolute configuration of chiral molecules, even when only 1 mg or less of a given compound is available (Warnke and Furche, 2012).

An ethnobotanical study carried out in Tanzania, which included screening of plant extracts for various biological activities, resulted in the selection of the plant *Ormocarpum kirkii* S. Moore (Papilionaceae) for further studies (Maregesi et al., 2007, 2010). Previous phytochemical investigation of *O. kirkii* has led to the isolation and identification of (1-3,11-3)-biflavanoids, some of which possessed antiplasmodial activity (Chhabra et al., 1990; Nyandat et al., 1990). This study focuses on the use of a platform which combines LC–MS and LC–SPE–NMR for the rapid separation and characterization of additional constituents from the same source material as used previously (Xu et al., 2011). Electronic circular dichroism (ECD) experiments in combination with NMR data were used to determine absolute configuration. These methods led to the identification of eight new and six known flavonoids and biflavanoids.

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2. Results and discussion

Our previous work focused on the isolation and identification of compounds from the chloroform fraction and the 8th ethyl acetate fraction (EA08) of a methanol extract of powdered *O. kirkii* root (Xu et al., 2011). In this work, the 5th and 6th ethyl acetate fractions (EA05 and EA06) were investigated, and some minor additional constituents of fraction EA08 were also identified.

In LC–MS, three peaks were observed in fraction EA05. These compounds were separated and collected using LC–SPE–NMR. By comparison with reported NMR and MS data, compounds **1** and **2** were identified as 4''-hydroxydiphysolone (Dhooghe et al., 2010)

and (+)-chamaejasmin (Niwa et al., 1986), respectively (see Fig. 1). Compound **3** showed an HR-Q-TOF-MS molecular ion peak at m/z 557.1469 $[M+H]^+$, consistent with a molecular formula of $C_{31}H_{24}O_{10}$. The 1H NMR spectrum (Table 1) resembled that of 5,5''-di-*O*-methylidiphysin (Dhooghe et al., 2010) but the ^{13}C NMR spectrum displayed 31 carbon resonances instead of the 16 duplicated signals that appeared in the spectrum of 5,5''-di-*O*-methylidiphysin. These signals were ascribed to two carbonyl functions, 24 aromatic carbons, one methoxy and four methine carbons (Table 2). Typical signals for C-2, C-3, and C-4 were observed at δ_C 171.6 and 171.8, 44.4 and 44.5, 37.2 and 37.4, respectively. It was therefore concluded that compound **3** was a (1-3,II-3)-bis-dihydrocoumarin, with

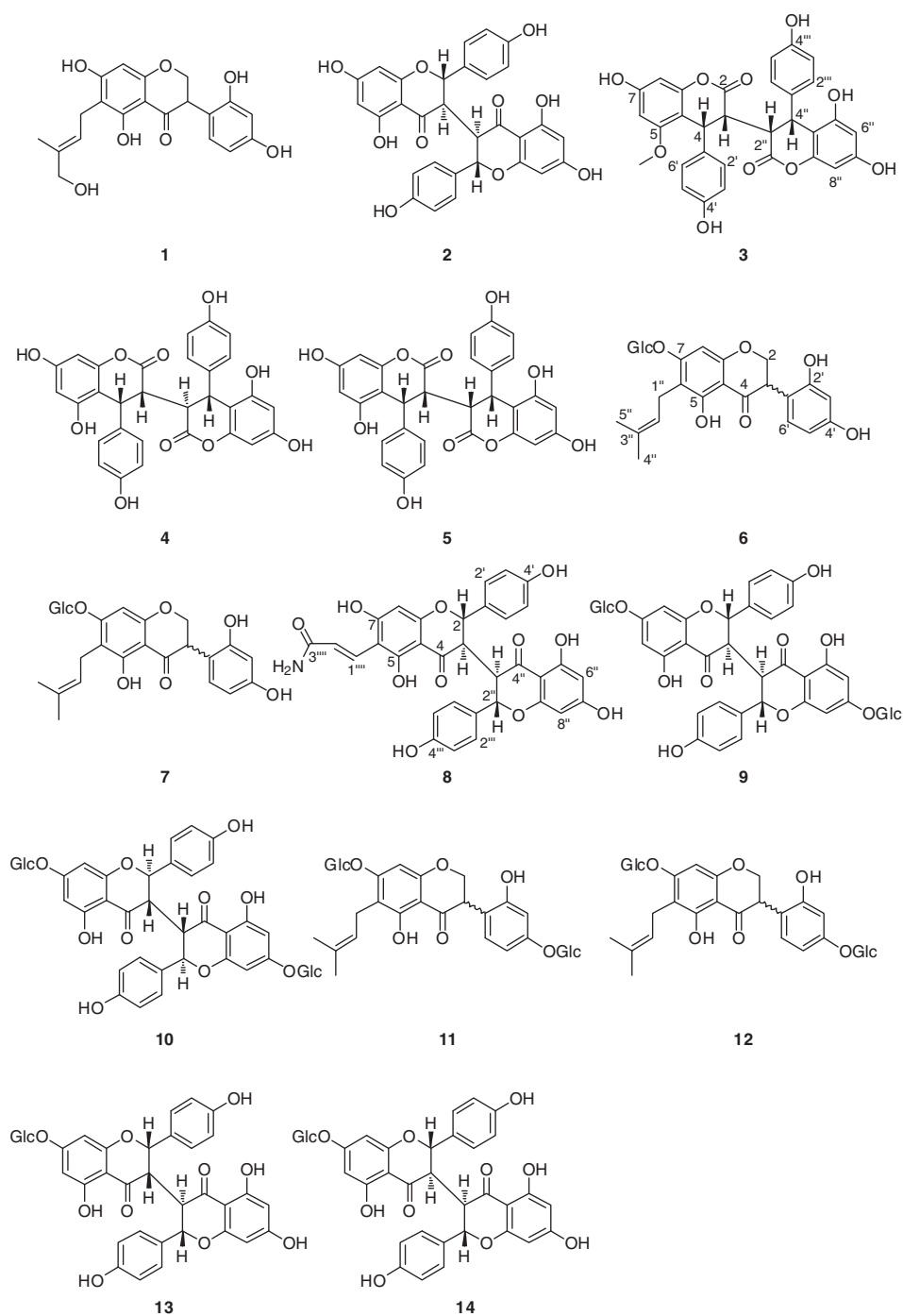


Fig. 1. The structure of compounds from *Ormocarpum kirkii*.

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