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Short communication

Iridoid and phenylethanoid glycosides from *Heterophragma sulfureum*

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ABSTRACT

An unusual iridoid diglycoside (specioside 6′-*O*-α-D-galactopyranoside) and a new phenylethanoid triglycoside (heterophragmoside) were isolated from the leaves and branches of *Heterophragma sulfureum* together with specioside, verminoside, 6-*trans*-feruloylcatapol, stereospermoside, (−)-lyoniresinol 3α-*O*-β-D-glucopyranoside, (+)-lyoniresinol 3α-*O*-β-D-glucopyranoside, (−)-5′-methoxyisolariciresinol 3α-*O*-β-D-glucopyranoside, (+)-5′-methoxyisolariciresinol 3α-*O*-β-D-glucopyranoside, and dehydroconiferyl 4-*O*-β-D-glucopyranoside. The structural elucidations were based on analyses of chemical and spectroscopic data.

1. Introduction

The family Bignoniaceae consists of about 120 genera and 800 species. They are mostly distributed in the tropical and subtropical of the old and new world regions. In Thailand, 12 genera and 24 species have been reported as indigenous plants, and several species are imported and cultivated as ornamental purposes (Santisuk, 1987; Srisanga et al., 2003). As part of our further systematic studies on plants from this family (Kanchanapoom et al., 2001, 2002a,b, 2006; Sinaphet et al., 2006), we investigated the constituents of *Heterophragma sulfureum* Kurz. (Thai name: Rang-Raeng), being collected from Khon Kaen province, Thailand. *H. sulfureum* is a tree up to 25 m high, distributed in Thailand, Myanmar, Laos and Cambodia. The flowers of this plant are used in north-eastern part of Thailand as vegetable for cooking purpose. The leaves are used for external treatment of skin diseases. The phytochemical investigation has not been reported on this species. The present paper deals with the isolation of 11 compounds from *n*-BuOH fraction of the MeOH extract of the leaves and branches of this plant, including an unusual new iridoid diglycoside with α-galactose substitution (**2**) and a new phenylethanoid triglycoside (**6**), as well as four known iridoid glucosides (**1**,**3–5**), four known lignan glucosides (**7–10**), and a neolignan glucoside (**11**).

2. Results and discussion

The methanolic extract of *H. sulfureum* was partitioned with solvents of increasing polarity. The *n*-BuOH soluble fraction was subjected to highly porous copolymer resin of styrene and divinylbenzene (Diaion HP-20), silica gel, RP-18, preparative HPLC-ODS column chromatography to afford 11 compounds (**1**–**11**), of which compounds **2** and **6** were new. Nine known compounds were assigned as specioside (**1**) (Compadre et al., 1982), verminoside (**3**) (Sticher and Afifi-Yazar, 1979), 6-*trans*-feruloylcatapol (**4**) (Stuppner and Wagner, 1989), stereospermoside (**5**) (Kanchanapoom et al., 2006), (−)-lyoniresinol 3α-*O*-β-D-glucopyranoside (**7**), (+)-lyoniresinol 3α-*O*-β-D-glucopyranoside (**8**), (−)-5′-methoxyisolariciresinol 3α-*O*-β-D-glucopyranoside (**9**), (+)-5′-methoxyisolariciresinol 3α-*O*-β-D-glucopyranoside (**10**) (Achenbach et al., 1992), and dehydroconiferyl 4-*O*-β-D-glucopyranoside (**11**) (Yoshizawa et al., 1990) by comparison of physical data with literature values and from spectroscopic evidence (Fig. 1).

Compound **2**, $[\alpha]_D^{24} - 60.5$, was isolated as an amorphous powder. Its molecular formula was determined as $C_{30}H_{38}O_{17}$ by negative HR-FAB mass spectrometric analyses. Inspection of the ^1H and ^{13}C NMR spectra indicated that this compound is an iridoid glycoside, closely related to specioside (**1**). In addition, the signals

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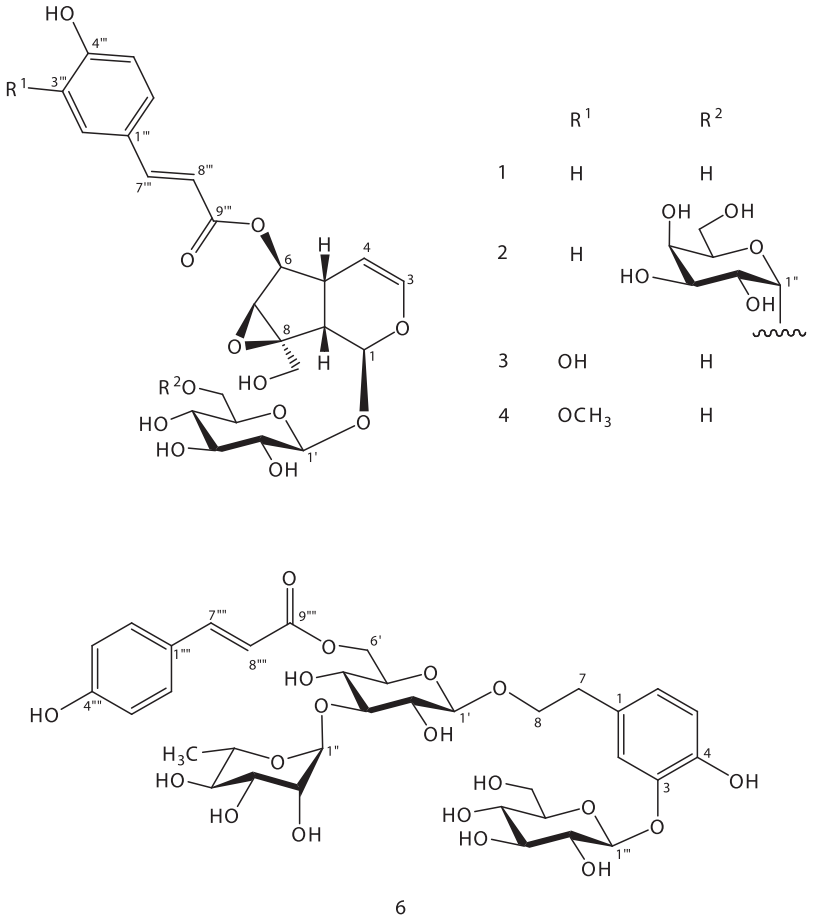

Fig. 1. Structures of compounds **1**–**4** and **6**.

of one sugar unit were observed in the ^{1}H and ^{13}C NMR spectra, deduced from an anomeric proton at δ_H 5.46 (d, J = 3.6 Hz) and six more carbon atoms at δ_C 100.2, 72.8, 71.6, 70.8, 70.3 and 62.5 (in C_5D_5N). The anomeric proton signal appeared as doublet with the coupling constant, J = 3.6 Hz, suggesting that this sugar moiety was in an α-form. This sugar part could be assigned to be α-D-galactopyranosyl moiety, based on the detailed analysis of COSY and HMQC experiments as well as the splitting patterns of each

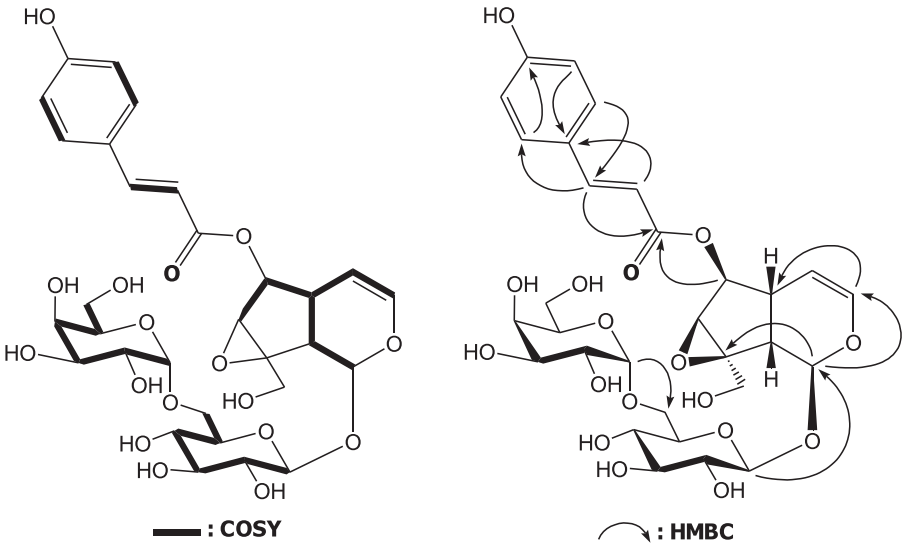

Fig. 2. COSY and HMBC correlations of compound **2**.