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Colchicinoid glucosides from seedless pods of Thai origin *Gloriosa superba*

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ABSTRACT

Three new colchicinoid glucosides, dongduengosides A-C were isolated from seedless pods of Thai origin *Gloriosa superba* together with colchicoside, colchicine, 2-demethylcolchicine and luteolin 7-*O*-β-D-glucopyranoside. In addition, colchicine, 2-demethylcolchicine, 3-methylcolchicine, colchicoside, *epi*-catechin and quercetin 3-*O*-β-D-glucopyranoside were identified from seeds. The structure determinations were based on physical data and spectroscopic evidence including 1D- and 2D-experiments. This study showed that the different part of seedless pods and seeds provided the major difference in compounds.

1. Introduction

Gloriosa superba L. (Thai name: Dong-Dueng), a member of the family Colchicaceae, is an herbaceous climber native of tropical Africa, and commonly growing in tropical regions of Asia. In Thailand, this species is described as a toxic plant since there was report on several cases of apparent poisoning related to consumption of its tubers. This plant is well known to contain colchicinoid derivatives such as colchicine, colchicoside, and lumicolchicine (Dunuwille et al., 1968; Chaudhuri and Thakur, 1993; Joshi et al., 2010). Furthermore, the medicinal uses, biological activities and toxicological investigations have been reviewed (Jana and Shekhawat, 2013). This present study deals with the isolation and determination of the chemical constituents from seedless pods and seeds, including three new colchicinoid glucoside (**2–4**), four known colchicinoids (**1**, **5–7**), and three flavonoids (**8–10**).

2. Results and discussion

The methanolic extracts of seedless pods and seeds were processed individually by a combination of chromatographic procedures to provide ten compounds (**1-10**). From seedless pods, three new colchicinoid glucosides (**2–4**) were identified (Fig. 1). Seven known compounds were identified as colchicine (**5**), 2-demethylcolchicine (**6**), 3-demethylcolchicine (**7**) (Hufford Hufford et al., 1979), colchicoside (**1**) (Yoshida et al., 1988), *epi*-catechin (**8**) (Agrawal et al., 1989), quercetin 3-*O*-β-D-glucopyranoside (**9**) and luteolin 7-*O*-β-D-glucopyranoside (**10**) (Agrawal and Bansal, 1989) by comparison of physical data with literature values and from spectroscopic evidence.

Dongduengoside A (**2**) was isolated as an amorphous powder. The molecular formula was determined to be $C_{26}H_{31}NO_{11}$ by high resolution electrospray time-of-flight (HR-ESI-TOF) mass spectrometric analysis. Inspection of the ^{1}H and ^{13}C NMR spectra revealed the presence of two methoxyl groups and one β-D-glucopyranosyl unit in addition to the signals of a colchicinoid skeleton as compared to colchicoside (**1**). The spectroscopic data were related to those of colchicoside (**1**) except for lacking one methoxyl signal, which established the presence of a hydroxyl group. The locations of these functional groups were assigned by the results of 2D-NMR experiments. All protonated carbons were assigned by HSQC experiment. An NOESY correlation between the anomeric proton signal at δ_H 4.71 (d, J = 7.2) and H-4 at δ_H 6.80 (*s*), as well as the

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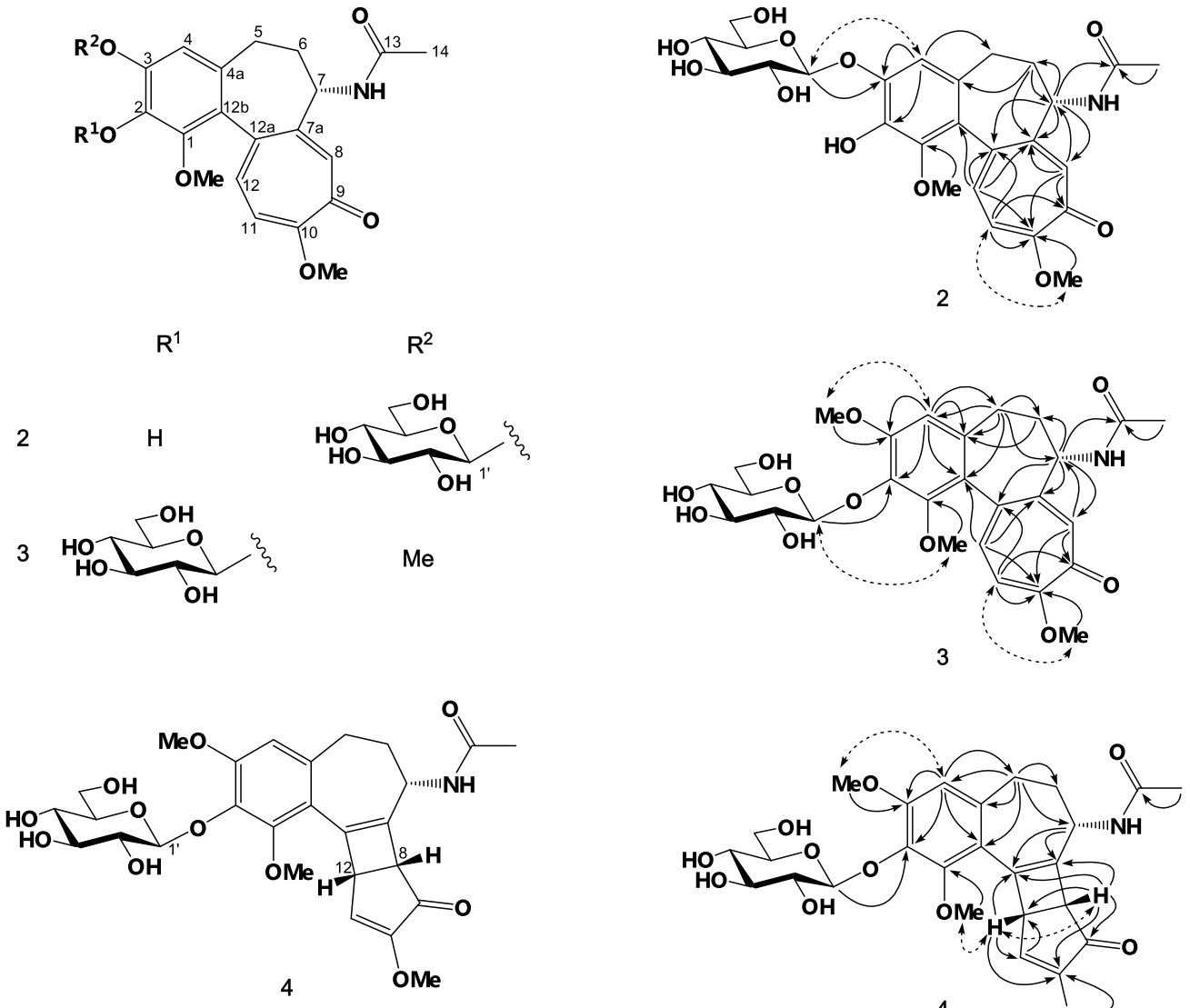

Fig. 1. Structures of compounds **2–4**.

Fig. 2. HMBC and NOESY correlations of compounds **2–4**.

HMBC correlations from both protons to C-3 (δ_C 146.0) were observed from the spectra, indicating that the glucopyranosyl unit was placed at C-3 position. Two methoxyl groups at δ_H 3.50 with δ_C 60.1 and δ_H 3.86 with δ_C 56.1 were ascribable to be 1-OMe and 10-OMe, from the HMBC correlations to C-1 (δ_C 145.1) and C-10 (δ_C 163.5), respectively (Fig. 2). Thus, the remaining hydroxyl group could be deduced to be linked to C-2 position (δ_C 139.0). Consequently, the structure of compound **5** was elucidated to be 2-demethylcolchicoside or 2,3-didemethylcolchicine 3-*O*-β-D-glucopyranoside.

Dongduengoside B (**3**) was obtained as an amorphous powder and its molecular formula was determined to be $C_{27}H_{33}NO_{11}$ by high resolution electrospray time-of-flight (HR-ESI-TOF) mass spectrometric analysis. The ^{1}H and ^{13}C NMR spectroscopic data were closely related to those of colchicoside (**1**). The significant differences were the chemical shifts of A-ring, suggesting the interchange of the functional groups. The complete assignments were clearly established by NOESY, HSQC and HMBC experiments. In the HMBC spectrum, the correlation was found from the anomeric proton at δ_H 4.97 (d, J = 7.3) to C-2 (δ_C 137.7), indicating the position of the sugar unit to this carbon atom. Also, three methoxyl groups at δ_H 3.44 with δ_C 60.8, δ_H 3.85 with δ_C 56.4, and δ_H 3.85 with δ_C 56.1 were assignable to be 1-OMe, 3-OMe and 10-OMe, respectively, by the observation of HMBC correlations as illustration in Fig. 2. Moreover, the NOESY spectrum showed the significant correlations from the anomeric proton to the 1-OMe, and from H-4 (δ_H 6.75) to 3-OMe, confirming the position of the sugar unit. Therefore, the structure of this compound was identified as 2-demethylcolchicine 2-*O*-β-D-glucopyranoside.

Dongduengoside C (**4**) was obtained as an amorphous powder. The molecular formula was identified to be $C_{27}H_{33}NO_{11}$ by its HR-ESI-TOF mass spectrometric analysis. The ^{1}H and ^{13}C NMR spectra showed the presence of three methoxyl groups, one β-D-glucopyranosyl unit in addition to the typical signals for colchicine lumi-derivatives as the core structure (Potešilová et al., 1985; Meksuriyen et al., 1988). The chemical shifts of this compound were related to those of β-lumicolchicine (Meksuriyen et al., 1988) except for a set of additional signals of a β-D-glucopyranosyl unit instead of one methoxyl group. The assignment of the structure was deduced by the results from 2D-NMR spectroscopic methods including NOESY, HSQC and HMBC experiments. The sugar unit was assigned to be located at C-2 (δ_C 136.2) since the HMBC