Note

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Glucose esters of caffeic acid from *Allium macrostemon* Bunge

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Abstract

Two new glucose esters of caffeic acid, 1-*O*-(*E*)-caffeoyl-β-D-glucopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranose (allimacronoid A-2, 1) and 1-*O*-(*E*)-caffeoyl-{β-D-glucopyranosyl-(1→4)-[β-D-glucopyranosyl-(1→2)]}-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranose (allimacronoid B-2, 2) were isolated from the leaves of *Allium macrostemon* Bunge. The chemical structures were elucidated based on the analyses of the spectroscopic and chemical data.

Keywords : Amaryllidaceae, *Allium macrostemon*, caffeic acid, allimacronoid A-2, allimacronoid B-2

I Introduction

Allium macrostemon Bunge (Amaryllidaceae), known as wild onion, is widely distributed in East Asian countries. In Japan, the species is well known edible weed like other *Allium* species such as onion (*A. cepa* L.), garlic (*A. sativum* L.) and Welsh onion (*A. fistulosum* L.), *etc.* Some steroidal saponins have been isolated from the bulb [1], which showed various biological activities [2-5] such as acute myocardial ischemia, hyperglycemia, hyperlipidemia and visceral obesity, *etc.* Nakane *et. al.* reported the isolation and HPLC analysis of the flavonol glycoside constituents in the aerial part (leaf) of this plant [6]. Recently, Usui *et al.* also isolated ferulic acid glucosides (1-*O*-(*E*)-feruloyl-β-D-glucopyranoside [7], 1-*O*-(*E*)-feruloyl-β-D-gentiobioside [7], tuberonoid A [8, 9], allimacronoids A-D [7, 9]), 1-*O*-(*E*)-caffeoyl-β-D-sophoroside [10] and kaempferol glycosides [10] from the leaves of this species. In continuing systematic studies on the chemical constituents of *A. macrostemon* [11-13], two new caffeic acid esters with oligo-glucose (1 and 2) were isolated from the leaves of the plant. The chemical structures of these compounds were elucidated from their spectroscopic and chemical data.

II Results and Discussion

A new compound 1 gave NH_4 adduct ion peak at *m/z* 684.2347 $[M+NH_4]^+$, which corresponded to the molecular formula of $C_{27}H_{38}O_{19}$. The ^{1}H-NMR spectrum of 1 showed ABX-type (δ 6.78, J=8.0 Hz, 1H; δ 6.99 J=1.9, 8.0 Hz, 1H and δ 7.07, J=1.9 Hz, 1H) aromatic proton signals together with *trans*-olefinic (δ 6.31 and 7.65, J=15.8 Hz, each 1H) signals suggesting the presence of a caffeic acid moiety [10]. Acid hydrolysis of 1 with 0.5 N HCl yielded *trans*-caffeic acid which was identified by HPLC analysis. The ^{1}H-NMR spectrum showed three sugar anomeric (δ 5.69, J=7.8 Hz, δ 4.58, J=7.8 Hz and δ 4.32, J=7.8 Hz) proton signals. In the ^{13}C-NMR spectrum of 1 (Table 1), sugar signals (18 carbons) were also observed supporting the presence of three hexose moieties which were identified as D-glucose by TLC and HPLC analyses. These ^{1}H- and ^{13}C-NMR data of 1 were almost identical to those of allimacronoid A [9] without only one methyl signal arising from ferulic acid unit of allimacronoid A. The characteristically downfield shifts of H-1 (δ 5.69) and H-6 (δ 4.16) signals observed in the ^{1}H-NMR spectrum (Table 1) suggested the pattern of the presence of the linkages between glucose C-1 - caffeic acid C-9, glucose C-2 - glucose C-1' and glucose C-6 - glucose C-1" [7, 9, 10]. These spectral data,

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