SHORT COMMUNICATION

Chemical constituents isolated from Zygophyllum melongena Bunge growing in Mongolia

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ABSTRACT
We report the first investigation of the chemical constituents of Zygophyllum melongena Bunge, a species growing in Mongolia. The quinovic acid glycosides 3-O-[(β-D-glucopyranosyl)quinovic acid and 3-O-[(β-D-glucopyranosyl)quinovic acid (28→1)-(β-D-glucopyranosyl) ester were identified in the chloroform fraction along with the flavonoid glycoside astragalin. The n-butanol fraction contained (+)-D-pinitol as the major component, a cyclitol with anti-diabetic properties. The structures of the isolated natural products were confirmed using ESI-MS and NMR spectroscopy (1H, 13C, COSY, HSQC, HMBC, NOESY and ROESY). This is the first report of the isolation of (+)-D-pinitol from the genus Zygophyllum.

1. Introduction
Zygophyllum melongena is a medicinal plant belonging to the flowering plant family Zygophyllaceae. The genus Zygophyllum is represented by about 150 species growing in deserts and steppes from the Mediterranean to Central Asia, South Africa and Australia. Twelve species of Zygophyllum are known members of the flora of Mongolia (Grubov 1982; Ligaa et al. 2006; Ayad et al. 2012). In the scientific literature as well as in folk medicine,
Zygophyllum species are known as medicinal plants and their medicinal values are well documented (Grubov 1982; Ligaa et al. 2006; Ayad et al. 2012).

2. Results and discussion

Herein, we describe for the first time the isolation and structural elucidation of four compounds from *Z. melongena*: 3-O-(β-D-glucopyranosyl)quinovic acid (1), 3-O-(β-D-glucopyranosyl)quinovic acid (28→1)-(β-D-glucopyranosyl) ester (2), astragalin (3) and (+)-D-pinitol (4) (Figure 1). The quinovic acid glycosides 1 and 2 and the flavonoid glycoside 3 were obtained from the chloroform fraction, whereas (+)-D-pinitol (4), a cyclitol with anti-diabetic properties, was the major component of the n-butanol fraction.

Compound 1 was obtained as colourless crystals. Its molecular weight was found to be 648 g/mol, and the molecular formula was C_{36}H_{56}O_{10} based on mass and ^{13}C NMR spectra. Based on the ^{1}H and ^{13}C NMR data of compound 1 (Table S1) supported by analysis of the two-dimensional NMR spectra (Figures S1–S15) and a comparison with the corresponding values reported in the literature (Aquino et al. 1988; Ahmad et al. 1993; Zi-jun et al. 2011), the structure was identified as 3-O-(β-D-glucopyranosyl)quinovic acid (1). Compound 1 is an inhibitor of the snake venom phosphodiesterase-I (Fatima et al. 2002; Mostafa et al. 2006).

Compound 2 was isolated as colourless crystals. Its molecular formula was C_{42}H_{66}O_{15} corresponding to a molecular weight of 810 g/mol on the basis of mass and ^{13}C NMR spectra. By complete assignment of the ^{1}H and ^{13}C NMR data of compound 2 (Table S1) supported by the two-dimensional NMR spectra (Figures S16–S31) and a comparison with the corresponding values reported in the literature (Pizza et al. 1987; Aquino et al. 1988; Cerri et al. 1988; Aquino et al. 1989; Kang et al. 2004; Zhang et al. 2007; Zi-jun et al. 2011), the structure was assigned as 3-O-(β-D-glucopyranosyl)quinovic acid (28→1)-(β-D-glucopyranosyl) ester (2).

Compound 3 was isolated as a green amorphous solid. The mass spectrum combined with the ^{1}H and ^{13}C NMR data (Table S2) suggested a molecular formula of C_{21}H_{20}O_{11}. Based on analysis of the one- and two-dimensional ^{1}H and ^{13}C NMR data of compound 3 (Figures S32–S42) and comparison with the corresponding values reported in the literature (Davgadorj 1999; Chludil et al. 2008; Desai et al. 2014; Gauelyte et al. 2014; Zhang et al. 2015), the structure was assigned as kaempferol 3-O-(β-D-glucopyranosyl)quinovic acid (28→1)-(β-D-glucopyranosyl) ester (3).

Compound 4 was isolated as a colourless amorphous solid and proved to be optically active: [α]_D^{20} = 42.0, c 1.3, MeOH; [α]_D^{20} = 37.1, c 0.16, H_2O. The mass spectrum and the ^{13}C
NMR data (Table S2) indicated a molecular formula of C$_{7}$H$_{14}$O$_{6}$. Analysis of the $^1$H and $^{13}$C NMR data of compound 4 supported by the 2D NMR spectra (COSY, HMBC, HSQC and NOESY) (Figures S43–S49) led to the assignment as (+)-D-pinitol (4). The structure of compound 4 was also confirmed by comparison with literature data which have been reported for (+)-D-pinitol (4) (El-Youssef 2007; Jain et al. 2007; El-Youssef et al. 2008). (+)-D-Pinitol (4) is known for its anti-diabetic (Narayanan et al. 1987), anti-inflammatory (Singh et al. 2001) and feeding-stimulant activities (Numata et al. 1979). In the present report, (+)-D-pinitol (4) was isolated for the first time from the genus *Zygophyllum*.

3. Conclusions

No previous investigation concerning the chemical constituents of the Mongolian medicinal plant *Z. melongena* Bunge was reported. In the present work, we have isolated four compounds from the aerial parts of this plant. The quinovic acid glycosides 3-O-((β-D-glucopyranosyl)quinovic acid (1) and 3-O-((β-D-glucopyranosyl)quinovic acid (28→1)-((β-D-glucopyranosyl) ester (2) and astraqalin (3), a flavonoid glycoside, were identified in the chloroform fraction. On the other hand, large amounts of (+)-D-pinitol (4), a cyclitol with anti-diabetic properties, were isolated from the n-butanol fraction. This is the first report for the isolation of (+)-D-pinitol (4) from the genus *Zygophyllum*. From 4.0 kg of dried plant material of *Z. melongena*, an amount of 3.49 g of (+)-D-pinitol (4) was obtained. Thus, we conclude that the Mongolian medicinal plant *Z. melongena* is a major natural source for (+)-D-pinitol (4). The unequivocal structural assignments for the four compounds 1–4 are based on extensive NMR spectroscopic investigations ($^1$H, $^{13}$C, COSY, HSQC, HMBC, NOESY and ROESY). The isolation of the bioactive compounds 1–4 from *Z. melongena* may help to explain the pharmacological properties of this plant.

Supplementary material

Supplementary material to this article is available online: Experimental details, Tables S1 and S2 and Figures S1–S49 ($^1$H NMR, $^{13}$C NMR, COSY, HSQC, HMBC and NOESY spectra of the compounds 1–4). A voucher specimen of *Zygophyllum melongena* Bunge has been deposited at the herbarium of the Ulaanbaatar Institute of Botany, Mongolian Academy of Sciences (voucher number: chl.08.2010).

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Disclosure statement

No potential conflict of interest was reported by the authors.
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