SHORT COMMUNICATION

A new triterpenoid glycoside from the leaves and stems of *Duranta repens*

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A new triterpenoid glycoside (I) was isolated from the methanol extract of the leaves and stems of *Duranta repens* L. (Verbenaceae) along with 14 known compounds consisting of eight triterpenoids, four iridoids, one phenylethanoid glycoside and one flavonoid. The chemical structure of I was determined to be bayogenin 3-\(O-\beta-D\)-glucopyranoside]-28-\(O\)-\(\alpha-L\)-rhamnopyranosyl-(1→5)-\(O\)-\(\beta-D\)-apiofuranosyl-(1→4)-\(O\)-\(\alpha-L\)-rhamnopyranosyl-(1→2)-\(O\)-\(\alpha-L\)-arabinopyranosyl] ester, based on spectroscopic data. In addition, the inhibitory effects of the isolates on lipoxygenase activity were examined. Among them, acteoside and apigenin resulted in 94\(^\pm\)3.6\% and 82\(^\pm\)4.7\% inhibition, respectively, at 0.5 mM.

**Keywords:** *Duranta repens*; Vabenaceae; triterpenoid glycoside; lipoxygenase inhibitory effect

Introduction

*Duranta repens* L. is a Verbenaceae plant native to South America, and is primarily cultivated as an ornamental plant in Japan. The fruits and leaves of this plant were used for the treatment of malaria and abscess, respectively, in China (Takeda et al. 1995). With regard to the chemical constituents of this plant, iridoids (Kuo et al. 1996; Shahat et al. 2005), diterpenoids (Anis et al. 2001; Ahmad et al. 2009), phenylethanoid glycosides (Kuo et al. 1996; Shahat et al. 2005; Ahmad et al. 2009), flavonoids (Anis et al. 2001, Anis et al., 2002; Iqbal et al. 2004; Ahmad et al. 2009), triterpenoids (Kuo et al. 1996; Shahat et al. 2005; Hiradate et al 1999; Castro et al 1997; Ahmed et al. 2009), isoprenylated acetophenone derivative (Anis et al. 2002) and coumarinolignoids (Ahmad et al. 2009) were isolated. In the course of our studies on the constituents and biological activities of Verbenaceae plants (Ono, Furusawa,
et al. 2013a), we examined the methanol (MeOH) extract of the leaves and stems of *D. repens* ‘Takarazuka’. This report deals with the isolation and structural characterisation of a new triterpenoid glycoside along with 14 known compounds consisting of eight triterpenoids, four iridoids, one phenylethanoid glycosides and one flavonoid from the extract. In addition, the lipoxigenase inhibitory effects of the MeOH extract and isolates are also described herein as an inflammation model.

**Results and discussion**

The leaves and stems of *D. repens* were extracted with MeOH. This extract was partitioned between 90% MeOH and hexane. The former fraction was successively subjected to silica gel, Chromatorex ODS and Sephadex LH-20 column chromatography, as well as HPLC on ODS to yield 1–15.

Compounds 2–15 were identified as taccasoside C (2) (Castro et al. 1997), taccasoside B1 (3) (Castro et al. 1997), durantain I (4) (Hiradate et al. 1999), durantain III (5) (Hiradate et al. 1999), durantain II (6) (Hiradate et al. 1999), mi-saponin B (7) (Kitagawa et al. 1975; Verotta et al. 1996), ursolic acid (8) (Ono et al. 2004), oleanolic acid (9) (Mahato & Kundu 1994), lamiide (10) (Junior 1985; Ono et al. 2006), durantoside I (11) (Sasaki et al. 1989), duranterecitoside B (12) (Takeda et al. 1995), duranterecitoside A (13) (Takeda et al. 1995), acteosie (14) (Sasaki et al. 1989; Ono, Furusawa, et al. 2013a), and apigenin (15) (Ono et al. 2008), respectively, based on their physical and spectral data (Figure 1).

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Compound 1 was obtained as an amorphous powder, and its molecular formula was analysed as C$_{58}$H$_{94}$O$_{26}$ by a combined analysis of its negative and positive HR-ESI-MS spectra, which showed an [M–H]$^-$ ion peak at *m/z* 1205.59455 (Calcd for C$_{58}$H$_{93}$O$_{26}$: 1205.59403) and an [M + Na]$^+$ ion peak at *m/z* 1229.59403 (Calcd for C$_{58}$H$_{94}$O$_{26}$Na: 1229.59310), respectively (Figures S1 and S2). On acidic hydrolysis, 1 afforded D-apiose, L-arabinose, L-rhamnose and D-glucose. Identification of the monosaccharides, including their absolute configurations, was performed on direct HPLC analysis of the hydrolysate using an optical rotation detector. The $^1$H NMR spectrum of 1, which was similar to that of 4, exhibited signals due to six tertiary methyl groups, two secondary methyl groups assignable to H$_{3}$-6 of 6-deoxyhexosyl units and five anomeric protons. The $^{13}$C NMR data, glycosylation shifts (Kasai et al. 1977; Ishii et al. 1981; Ono, Ochiai, et al. 2013b) and coupling constants of signals due to anomeric and methine protons and the chemical shifts of $^{13}$C NMR data, glycosylation shifts (Kasai et al. 1977; Tori et al. 1977; Fujioka et al. 1989; Ono et al. 2007, 2011) were observed at C-2 of Ara, C-4 of Rha, C-5 of Api and C-3 of Agl. Further, key HMBC correlations were observed between H-1 of Glc and C-3 of Agl, H-1 of Ara and C-28 of Agl, H-1 of Rha and C-2 of Ara, H-1 of Api and C-4 of Rha, and H-1 of Rha and C-5 of Api (Figure S9). In addition, positive FAB-MS exhibited a fragment ion peak at *m/z* 673 [1303–146 (deoxyhexosyl unit) × 2–132 (pentosyl unit)]$^+$ (Figure S10). Finally, the assigned NMR data of the aglycone moiety and the sugar moiety were considerably similar to those of 3 and 4, respectively. Consequently, 1 was determined to be bayogenin 3-O-[β-D-glucofuranosyl]-28-O-[α-L-
In a pilot study, the MeOH extract from this plant demonstrated apparent lipoxygenase inhibition with 26 μg/mL of IC\textsubscript{50} value. To gain insight, the active constituents 1–15 herein were assayed. Among them, 14 and 15 demonstrated 94.0 ± 3.6% and 82.2 ± 4.7% inhibition, respectively, at a concentration of 0.5 mM. However, the effects of the other compounds were less than 25% (Table S4). In a parallel experiment, a positive control [nordihydroguairetic acid (NDGA)] showed 96.2 ± 3.1% of the inhibitory effect.

**Conclusion**

In this study, we isolated and elucidated the structures of 15 compounds from the MeOH extract of the leaves and stems of *D. repens* ‘Takarazuka’. Among them, one compound was a new triterpenoid glycoside. In addition, the MeOH extract and two aromatic compounds

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**Figure 1.** Structures of 1–15.
demonstrated lipoxygenase inhibitory effect. This result may indicate usefulness of *D. repens* in treatment of inflammation.

**Supplementary material**

Supplementary material relating to this article is available online, alongside Tables S1–S6, Figure S9, and NMR spectra and MS (Figures S1–S8, S10) of 1 at [http://dx.doi.org/10.1080/14786419.2015.1046870](http://dx.doi.org/10.1080/14786419.2015.1046870).

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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