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Iridoids, monoterpenoid glucoindole alkaloids and flavonoids from *Vinca major*

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We would like to dedicate this manuscript to "60th birthday of Prof. Olov Sterner" who is my PhD co-supervisor and former boss from Lund University, Sweden.

Keywords:
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Secoiridoid
Vinmajoroside
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ABSTRACT

A new secoiridoid glucoside, vinmajoroside (**1**), was isolated from the leaves of *Vinca major* L. along with 11 known compounds belonging to the secoiridoid ((7α)-7-*O*-methyl-morroniside, **2**), iridoid (loganin, loganic acid and 7-*O*-*p*-coumaroylloganin), monoterpenoid glucoindole alkaloid (5 (*S*)-5-carboxyvincoside and strictosamide), flavonoid (rutin, kaempferol 3-O-rutinoside and robinin), lignan (syringaresinol 4-*O*-β-glucopyranoside) and phenolic acid (chlorogenic acid) groups. The structure elucidation of the isolates was accomplished by extensive 1D and 2D-NMR experiments as well as ESI-MS. Secoiridoids and lignan were encountered for the first time in the genus *Vinca*.

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1. Subject and source

The genus *Vinca* L. (Apocynaceae) contains perennial subshrubs or herbaceous species distributed from Europe to North-west Africa, and South-west Asia. In the flora of Turkey, four species of the genus *Vinca* grow wild including *Vinca major* (Stearn, 1978; Koyuncu, 2011). Some of these species are utilized as laxative, diuretic, appetite stimulant and antipyretic in Anatolian folk medicine (Baytop, 1999). *V. major* (large periwinkle) is an herbaceous perennial plant that possesses both medicinal and ornamental values. Leaves of *V. major* L. were collected from Yeditepe University Campus, Kayisdagi, Istanbul, Turkey, in May 2010. The plant material was identified by one of us (Dr. H. Kirmizibekmez). The voucher specimen (YEF 10016) has been deposited at the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Yeditepe University, Istanbul, Turkey.

2. Previous work

Previous studies revealed the presence of alkaloids (Atta-Ur-Rahman et al., 1995), flavonoids (Sakushima and Nishibe, 1988) as well as one iridoid glycoside (loganic acid) (Bianco et al., 1984) as the secondary metabolites of the title plant.

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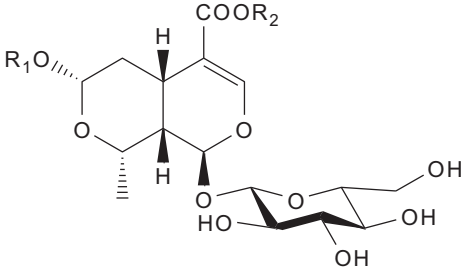
In the course of our phytochemical work on Turkish medicinal plants, we have investigated the secondary metabolite profile of *V. major*. This paper deals with the isolation and structure elucidation of a new secoiridoid, vinmajoroside (**1**) along with 11 known constituents as well as their chemotaxonomic significance.

3. Present study

The air-dried and powdered leaves of *V. major* (480 g) were extracted with MeOH (1.750 ml × 2) at 45 °C for 4 h. The combined methanolic extracts were concentrated to a residue (90 g) under reduced pressure. The extract was dissolved in MeOH–H_2O mixture (8:2) (100 ml), and then extracted with equal volumes of *n*-hexane (100 ml × 3). After removal of the MeOH, the partition went on with $CHCl_3$ (100 ml × 3) and *n*-BuOH (100 ml × 3) respectively. The *n*-BuOH-soluble portion was lyophilized (11 g) and applied to polyamide column (100 g) eluting with H_2O (200 ml) and a stepwise gradient of MeOH in H_2O (10–100% in steps of 10%, each 100 ml) to yield nine fractions, A–I. Fr. B (450 mg) was subjected to C_{18}-Medium Pressure Liquid Chromatography (C_{18}-MPLC, 2.5 × 55 cm) eluting with stepwise H_2O-MeOH gradient (0–20% MeOH, in steps of 5% of MeOH each 150 ml) to obtain frs.B_{1-5}. Purification of fr. B_2 (50 mg) by SiO_2 (9 g) CC ($CHCl_3$\MeOH\$H_2O$, 80:20:2, 75:25:5 and 70:30:3, each 100 ml) yielded loganic acid (17 mg). Fr. C (1.3 g) was rechromatographed over C_{18}-VLC (4 × 60 cm) eluting with stepwise H_2O–MeOH gradient (10–60%, in steps of 10% of MeOH each 200 ml) to afford subfractions C_{1-10}. Fr.C_4 (771 mg) was applied to a SiO_2 (90 g) column ($CHCl_3$\MeOH, 95:5 to 83:17, in steps of 3% of MeOH each 150 ml) to give loganin (15 mg). Fr. C_6 (440 mg) was similarly applied to SiO_2 (60 g) column ($CHCl_3$\MeOH\$H_2O$, 95:5:0.5, 90.10:1, 80:20:2 and 70:30:3, each 200 ml) and syringaresinol 4-*O*-*β*-glucopyranoside (5.4 mg) and frs.C_{6II-IV} were obtained. Further separation of fr. C_{6III} (120 mg) on a C_{18}-Vacuum Liquid Chromatography (C_{18}-VLC, 2.5 × 25 cm) by using stepwise H_2O–MeOH gradient (5–40% MeOH, in steps of 5% of MeOH each 100 ml) gave robinin (3 mg). Purification of 5 (*S*)-5-carboxyvincoside (23 mg) was accomplished by SiO_2 (8 g) CC ($CHCl_3$\MeOH\$H_2O$, 85:15:1.5, 80:20:2 and 75:25:2.5 each 50 ml) from subfraction C_{6III-B} (60 mg). Fr. C_9 (470 mg) was similarly applied to SiO_2 (60 g) column ($CHCl_3$\MeOH\$H_2O$, 95:5:0.5, 90:10:1, 85:15:1.5, 80:20:2, 70:30:3, each 250 ml) to yield frs.C_{9I-III}. Strictosamide was isolated from C_{9II} (78 mg) by C_{18}-VLC (2.5 × 25 cm, H_2O-MeOH gradient, 20–32% MeOH, 4% increasing MeOH) and SiO_2 ($CHCl_3$\MeOH, 95:5, 90:10, each 50 ml) CC successively. Fr. D (1.5 g) was subjected to C_{18}-MPLC eluting with stepwise H_2O-MeOH gradient (0–50% MeOH, 10% gradient each 400 ml) to obtain frs.D_{1-4}. Purification of fr. D_2 (69 mg) by SiO_2 (9 g) CC ($CHCl_3$\MeOH, 98:2 and 80:20, each 50 ml) afforded compound **1** (8.7 mg). Fr. D_3 (130 mg) was subjected to a SiO_2 (20 g) column using $CHCl_3$\MeOH (98:2 to 70:30 in steps of 3% of MeOH each 75 ml) gave **2** (16 mg). Fr F (400 mg) was applied to C_{18}-MPLC eluting with stepwise H_2O-MeOH gradient (5–40% MeOH in steps of 5% of MeOH each 100 ml) yielded chlorogenic acid (10 mg). Similarly, fr. G (1.75 g) was subjected to C_{18}-MPLC eluting with stepwise H_2O-MeOH gradient (5–60% MeOH, in steps of 5% of MeOH each 200 ml) and subfractions G_{1-8} were obtained. Purification of Fr G_4 (15.6 mg) by using a Sephadex LH-20 (8 g) CC MeOH (100 ml) yielded rutin (2.5 mg). Fr G_6 (70 mg) was chromatographed over Sephadex LH-20 CC (MeOH, 150 ml) to yield kaempferol 3-*O*-rutinoside (9 mg). Fr G_8 (55 mg) was separated by a SiO_2 (10 g) CC ($CHCl_3$\MeOH, 99:1 to 93:7, in steps of 1% of MeOH each 50 ml) to obtain 7-*O*-*p*-coumaroylloganin (9.2 mg).

The known compounds were identified as ((7*α*)-7-*O*-methylmorroniside) (**2**) (Hu et al., 2009), loganic acid (Zhang et al., 2003), loganin (Prasad et al., 2000), 7-*O*-*p*-coumaroylloganin (Houghton and Lian, 1986), 5 (*S*)-5-carboxyvincoside (Aimi et al., 1992), strictosamide (Faria et al., 2010), robinin (Yahara et al., 2000), rutin (Kazuma et al., 2003), kaempferol-3-*O*-rutinoside (Kazuma et al., 2003), syringaresinol-4-*O*-*β*-glucopyranoside (Park et al., 2010) and chlorogenic acid (Pauli et al., 1999) by comparison of their spectroscopic data with literature values (Fig. 1).

Compound **1** was obtained as an amorphous colorless powder. The ESI-MS of **1** exhibited a pseudomolecular ion at *m/z* 415, indicating a molecular formula of $C_{16}H_{24}O_{11}$ with 5 degrees of unsaturation. The ^{13}C NMR (Table 1) spectrum of **1** displayed 16 resonances six of which were arising from a *β*-glucose moiety. The remaining 10 signals (δ_C 172.9, 152.1, 113.6, 96.8, 94.9, 74.1, 40.2, 37.2, 32.4,19.9) together with one olefinic (δ_H 7.46), two hemiacetal (δ_H 5.82 and 4.82), one oxymethine (δ_H 3.97) two methine (δ_H 2.87–2.81 and 1.80–1.76) and one secondary methyl (δ_H 1.42) signals in the ^1H NMR spectrum (Table 1)



1 $R_1 = R_2 = H$
2 $R_1 = R_2 = Me$

Fig. 1. The structures of compounds **1** and **2**.

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