SHORT REPORT

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records of natural products

Secondary Metabolites of *Centaurea cadmea* Boiss.

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Abstract: Chlorogenic acid (**1**), scutellarin (**2**), syringin (**3**), 6S, 9R-roseoside (**4**) and *β*-sitosterol-3-*O*-*β*–D-glucopyranoside (**5**) were isolated from the aerial parts of *Centaurea cadmea* Boiss. (Asteraceae). Structure elucidation of the compounds were performed by using spectroscopic methods (1-D and 2-D NMR and LC-MS-MS). To the best of our knowledge, compounds **1**, **2**, **3** and **4** have been isolated for the first time from this endemic species. Compound **4** is new for the genus *Centaurea*.

Keywords: *Centaurea cadmea;* chlorogenic acid; scutellarin**;** syringin; roseoside; NMR.

1. Plant Source

Centaurea cadmea Boiss. belonging to section Phalolepis (Cass.) DC. (Asteraceae) with purple florets, is an endemic taxon for Anatolia, growing wild in N,W & SW of Turkey (1).

C. cadmea was collected from Denizli, Evrantepe, 1512 m, in June 2004 (37° 41' 18.6"N; 29° 00' 07'E) and identified by Prof. Dr. Ozcan Secmen, from Section of Botany, Department of Biology, Faculty of Science, Ege University, Izmir, Turkey. A voucher specimen was deposited in the Herbarium of Ege University, Faculty of Pharmacy, Izmir, Turkey (IZEF 5670).

2. Previous Studies

Ivalin, eupatorin, 5-hydroxy-3',4',6,7-tetramethoxyflavone, β-sitosterol and β-sitosterol-3-*O*-β-D-glucopyranoside have been isolated from *C. cadmea* (2). Hexadecanoic acid (%23.1) and carvacrol (%14.7) were detected as major compounds for the plant essential oil by GC and GC/MS (3). Antioxidant, antiinflammatory and antileishmanial activities of the *C. cadmea* have been reported before (4, 5).

3. Present Study

In the present study, dried and powdered aerial parts (600 g) were extracted sequentially with *n*-hexane and $CHCl_3$ and MeOH (3x10 mL/g, for each), sonicated at room temperature for 24h, and then

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filtered. The combined extracts were evaporated under reduced pressure to dryness at 40^0C. MeOH extract (53.51 g) was suspended in H_2O (300 mL) and partitioned with *n*-butanol (1.5 L). *n*-butanol extract (40 g) was then subjected to column chromatography (RP C-18 silica gel, 100% H_2O→100%MeOH with %10 increasing amount of MeOH) yielding Fractions A-R.

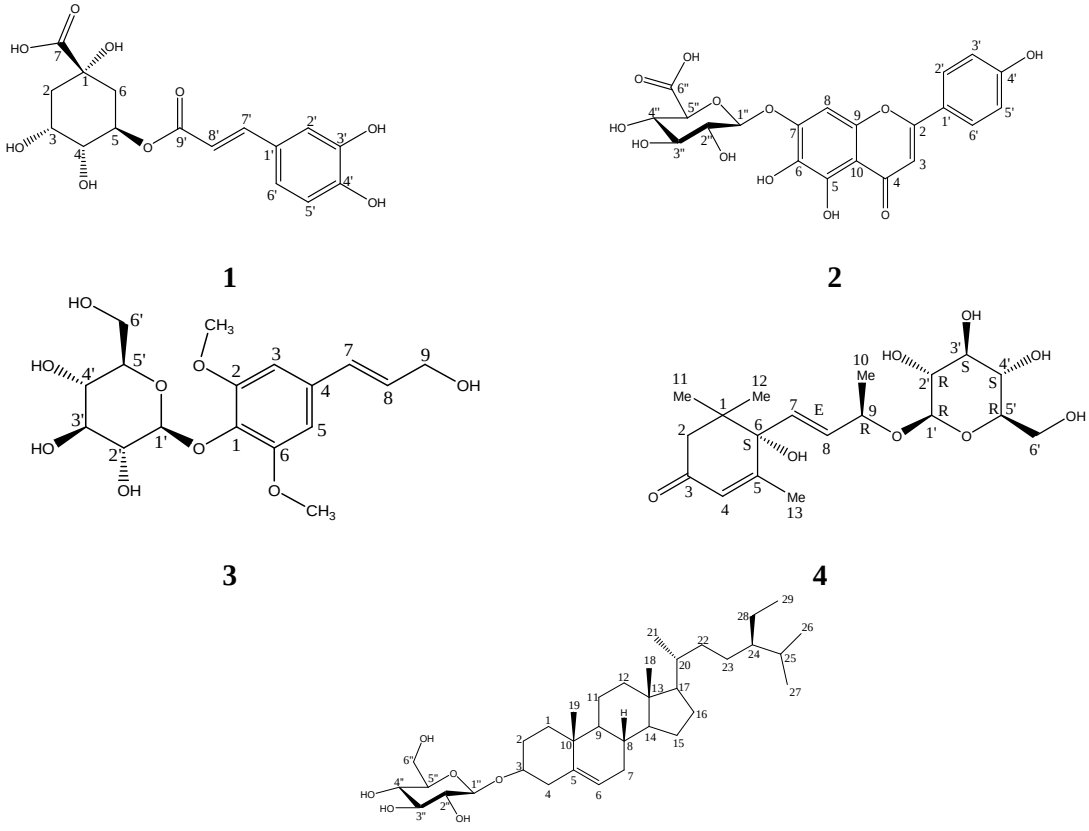

Figure 1. Structures of compound **1**-**5**.

Fraction C (4.8 g) was partitioned again with *n*-buthanol and water. *n*-buthanol fraction (1.5 g) was chromatographed over Sephadex LH-20 (100% MeOH) to afford 15 subfractions (Frs. C1-C15). Fraction C3 (269 mg) was re-subjected on Sephadex LH-20 (100% MeOH) to afford 8 subfractions (Frs C3a-C3h).

Fraction C3d (53 mg), further re-submitted on flash chromatography (RP C-18, MeOH/H_2O, 30:70→40:60 with 5% increasing amount of MeOH) to yield compound **1** (4 mg).

Fraction C4 (367 mg) was subjected to column chromatography (silica gel, $CHCl_3$/MeOH, 95:5→80:20 with 5% increasing amount of MeOH) and 11 subfractions were yielded (Frs. C4a-j). Fraction C4e (63-79) (28 mg) was submitted on column chromatography (silica gel, $CHCl_3$/MeOH, 90:10→88:12 with 2% increasing amount of MeOH) to afford 4 subfractions (Frs. C4e1-4). Fraction C4e2 was subjected on Sephadex LH-20 (100% MeOH) to afford 2 subfractions. Fraction C4e2a (10 mg), was further purified by preparative TLC ($CHCl_3$/MeOH/H_2O, 61:32:7) to afford compound A (6 mg). Besides re-chromatography of fraction C4f (12 mg) on preparative TLC ($CHCl_3$/MeOH/H_2O, 61:32:7) gave compound B (6 mg). Compound A and compound B was combined to give compound **2** (12 mg).

Fraction C11 (43 mg) was further re-chromatographed on prepacted column (RP C-18, 60 mL, %100 H_2O) to afford 4 subfractions (Frs. C11a-d). Fraction C11b (33 mg) was subjected to preparative TLC (silica gel, $CHCl_3$/MeOH/H_2O, 61:32:7) to afford compound **3** (19 mg).

Fraction C12 (8 mg) was also subjected to preparative TLC (silica gel, $CHCl_3$/MeOH/H_2O, 61:32:7) to give compound **4** (4 mg).

Fraction P (654 mg) was partitioned with EtOAc and water. EtOAc fraction (80 mg) was submitted on column chromatography (silica gel, $CHCl_3$/MeOH, 100:0→84:16 with 2% increasing amount of MeOH) to afford 5 sub-fractions (Frs. P1-P5). Fraction P4 (16 mg) was further re-chromatographed on prepacted column (silica gel, 12 mL, $CHCl_3$/MeOH, 95:5) to yield 2 subfractions. Fraction G4b (10 mg) was purified by prepacted column (silica gel, 20 mL, $CHCl_3$/MeOH, 100:0→96:4 with 1% increasing amount of MeOH) to yield compound **5** (7 mg).

Structures of the isolated compounds were determined on the basis of different spectroscopic techniques:1-D (1H ve 13C NMR) and 2-D NMR (COSY, HMQC ve HMBC) (Varian, 400 MHz) and LC-MS-MS (ESI) (Thermo-Quantum Access-Max) and comparison with the data those reported in literature (6-9).

Optical rotation of roseoside was done on Autopol I polarimeter in MeOH at 27^0C ($[\alpha]_D^{27}$= -21, c=00.1) (9). β-sitosterol-3-*O*-β-D-glucopyranoside were identified only by TLC comparison studies using pure reference compound.

Chlorogenic acid, scutellarin, syringin and 6S, 9R-roseoside were reported for the first time in *C. cadmea*. 6S, 9R-roseoside was also reported for the first time in *Centaurea* genus.

Acknowledgments

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