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FLAVONOID GLUCOSIDES FROM *Centaurea sphaerocephala*

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Centaurea sphaerocephala L., belonging to the tribe Cynarea of the Asteraceae family, is widespread in the entire Mediterranean region. Several medicinal uses have been reported for *Centaurea* species [1, 2]. Previous phytochemical studies of the species *Sphaerocephala* (ssp. *sphaerocephala* and ssp. *polyacantha*) led to the isolation of sesquiterpene lactones and lignans, sesquilignans, and dithienylacetylene [3, 4]. As part of our continuing phytochemical studies on *C. sphaerocephala* L. [5], we now report on the composition of the *n*-butanol soluble part of the aqueous-methanol extract of its aerial parts, which were collected during the flowering phase in May 2003 from EL Kala (East of Algeria) and authenticated by Prof. M. Kaabeche (Biology Department, University of Setif, Algeria) on the basis of Quezel and Santa [6]. A voucher specimen (CCS13/05/03) has been deposited in the Herbarium of the Biology Department of Mentouri University of Constantine. Leaves and flowers of *Centaurea sphaerocephala* L. (2170 g) were dried and macerated three times at room temperature with MeOH–H_2O (80:20 v/v) for 24 h. After filtration, the filtrates were combined, concentrated at room temperature and diluted with 850 mL H_2O. The resulting aqueous solution was extracted successively with $CHCl_3$, EtOAc, and *n*-BuOH. The organic layers were dried with Na_2SO_4, giving after removal of solvents under reduced pressure $CHCl_3$ (2.10 g), EtOAc (10.40 g), and *n*-BuOH (35.94 g) extracts. The *n*-butanol extract was applied to a column of silica gel (230–400 mesh) and eluted with chloroform–methanol with increasing polarity to yield 26 fractions (F_1–F_{26}). Fraction F_{13} submitted to preparative TLC on polyamide (toluene–methanol–methylethylketone, 4:3:3) and purified by preparative TLC on silica gel GF_{254} ($CHCl_3$–MeOH, 5:1) gave **1** (17 mg) and **2** (11 mg).

The structures of these compounds were established by UV, ^{1}H NMR, and MS analysis [7, 8]. The identity of the sugar moieties was confirmed by acid hydrolysis followed by co-chromatography with authentic samples. All these results were in good agreement with the respective literature data [9, 10].

Compound 1: $C_{22}H_{22}O_{11}$, yellow needles, mp 210°C; UV (MeOH, λ_{max}, nm): 268, 340; +NaOH: 267, 390; +$AlCl_3$: 268, 356; +$AlCl_3$/HCl: 275, 355, 385; +NaOAc: 250, 346; +NaOAc/H_3BO_3: 276, 348. ^{1}H NMR (250 MHz, MeOH-d_4, δ, ppm, J/Hz): 6.50 (1H, d, J = 2.2, H-6), 6.75 (1H, d, J = 2.2, H-8), 6.90 (1H, s, H-3), 6.95 (1H, d, J = 8.4, H-5′), 7.62 (1H, dd, J = 8.4; 2.2, H-6′), 7.72 (1H, d, J = 2.2, H-2′), 3.95 (3H, s, 3′-OMe), 5.20 (1H, d, J = 7.4, H-1″Glu), 3.40–4.20 (sugar protons). Mass spectrum (Positive FAB), *m/z* (I_{rel}, %): 485 $[M + Na]^+$ (38.33), 463 $[M + H]^+$ (11.66), 301 $[M + H – Glu]^+$ (6.66), 285 $[M + H – OGlu]^+$ (3.33).

This compound was characterized as 4′,5,7-trihydroxy-3′-methoxyflavone 7-*O*-*β*-glucoside (chrysoeriol 7-*O*-*β*-glucoside) [9].

Compound 2: $C_{21}H_{20}O_{10}$, yellow needles, mp 220°C; UV (MeOH, $\lambda_{max,}$ nm): 267, 333; +NaOH: 268, 368; +$AlCl_3$: 268, 337; +$AlCl_3$/HCl: 268, 337; +NaOAc: 271, 344; + NaOAc /H_3BO_3: 275, 342, 382. ^{1}H NMR (250 MHz, MeOH-d_4, δ, ppm, J/Hz): 6.35 (1H, d, J = 2.1, H-6), 6.50 (1H, d, J = 2.1, H-8), 6.65 (1H, s, H-3), 6.95 (2H, d, J = 8.6, H-3′, H-5′), 7.85 (2H, d, J = 8.6, H-2′, H-6′), 5.12 (1H, d, J = 7.5, H-1″Glu), 3.50–4.30 (sugar protons). Mass spectrum (Positive FAB), *m/z* (I_{rel}, %): 455 $[M + Na]^+$ (40.66), 433 $[M + H]^+$ (13.55), 271 $[M + H – Glu]^+$ (7.66), 255 $[M + H – OGlu]^+$ (2.66).

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This compound was characterized as: 4′,5,7-trihydroxyflavone 7-*O*-*β*-glucoside (apigenin 7-*O*-*β*-glucoside) [10]. All these compounds were isolated from C. *sphaerocephala* L. for the first time.

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