

SECONDARY METABOLITES FROM *Globularia alypum*

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The genus *Globularia* (Globulariaceae) includes two species in Algeria. One of them is endemic, *Globularia eriocephala* (Pomel); the other *Globularia alypum* L., widespread in the Mediterranean region [1], is used in folk medicine. Its leaves are traditionally used as a hypoglycemic agent, laxative [2], cholagogue, stomachic, purgative, and sudorific [3]. In the present paper we report on the qualitative and quantitative analysis of secondary metabolites extracted from the medicinal plant *G. alypum*, which has been the subject of several chemical and pharmacological investigations [4–10]. Aerial parts of *Globularia alypum* L. were collected during the flowering season in eastern Algeria (April 2004). A voucher specimen for this material (VAREN/ SB BF Rv /04/04) was deposited at the Herbarium of the Faculty of Sciences, University Mentouri-Constantine.

Air-dried and powdered aerial parts (1280 g) of *G. alypum* were macerated in an ethanolic solution (70%); the residue was filtered, concentrated, then successively extracted with petroleum ether, trichloromethane, ethyl acetate, and *n*-butanol. The AcOEt extract (10 g) was applied to a column of silica gel 60 and eluted with a gradient of CHCl₃–CH₃COCH₃ with increasing polarity. Preparative TLC on silica gel 60 F₂₅₄ using CHCl₃–acetone–acetic acid (4:0.25:0.25) led to luteolin, *para*-coumaric acid, and cinnamic acid, while using CHCl₃–acetic acid (4:0.25) led to apigenin.

The *para*-coumaric acid and cinnamic acid have already been isolated from this plant [4, 5]. Flavonic compounds were identified using UV and ¹H NMR spectra, chemical transformations, and comparison with authentic samples [11, 12]. Flavonoids **1**, **2** have been isolated previously from another species of *Globularia* [13], but from *G. alypum* L. this was the first time.

Apigenin, C₁₅H₁₀O₅, mp 348–350°C, UV (λ_{\max} , MeOH, nm): 268, 335; +NaOH: 274, 324, 392; +AlCl₃: 274, 300, 348, 382; AlCl₃/HCl: 274, 300, 334, 380; NaOAc: 276, 306, 380.

¹H NMR (250 MHz, CD₃COCD₃, δ , ppm, J/Hz): 7.90 (2H, d, J = 8.7, H-2', H-6'); 7.02 (2H, d, J = 8.7, H-3', H-5'); 6.65 (1H, s, H-3); 6.55 (1H, d, J = 2.2, H-8); 6.26 (1H, d, J = 2.2, H-6).

Luteolin, C₁₅H₁₀O₆, mp 329–331°C, UV (λ_{\max} , MeOH, nm): 264, 350; +NaOH: 267, 329, 402; +AlCl₃: 273, 303, 422; AlCl₃/HCl: 274, 297, 358, 385; NaOAc: 254, 269, 352.

¹H NMR (250 MHz, CD₃COCD₃, δ , ppm, J/Hz): 7.52 (1H, d, J = 2, H-2'); 7.49 (1H, dd, J = 8.4; 2, H-6'); 7.02 (1H, d, J = 8.4, H-5'); 6.62 (1H, s, H-3); 6.55 (1H, d, J = 2, H-8); 6.26 (1H, d, J = 2, H-8).

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