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SECONDARY METABOLITES FROM *Volutaria crupinoides*

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As a part of our ongoing program of research on Algerian Asteraceae [1–4], we report our results on *Volutaria crupinoides* (Desf.) Maire (Asteraceae), an endemic species to the Sahara [5]. This work concerned the phytochemical study of the chloroform and *n*-butanol soluble parts of the aqueous-ethanol extract of the leaves and flowers of *Volutaria crupinoides.*

Volutaria crupinoides was collected during the flowering stage in May 1998 in the Algerian Sahara and was authenticated by Pr. A. Kaabeche (University of Setif Algeria).

Air-dried leaves and flowers (1576 g) of *Volutaria crupinoides* were macerated in an EtOH solution (70%) for 24 hours three times. After filtration, the filtrate was concentrated (500 mL) and dissolved in H_2O (600 mL). The resulting solution was extracted successively with $CHCl_3$ and *n*-butanol. The organic phases were dried with Na_2SO_4 filtered, and concentrated under low pressure at room temperature to obtain the extracts: chloroform (12.4 g) and *n*-butanol (25.4 g).

The chloroform extract (6 g) was chromatographed on a silica gel (70–230 mesh) column eluted with a gradient of hexane–EtOAc to yield 12 fractions (F_1–F_{12}). Fraction F_6 (*n*-hexane–EtOAc 90:10) was subjected to preparative TLC on silica gel (*n*-hexane–EtOAc 50:50) to give compound **1** (55 mg).

The *n*-BuOH extract (14 g) was applied to a polyamid SC6 column eluted with a gradient of toluene–MeOH to yield 15 fractions (F_1–F_{15}). Fraction F_6 (toluene–MeOH 80:20) was purified by preparative TLC on polyamide (toluene–MeOH–methyl ethyl ketone 4:3:3) to give compound **2**. Fraction F_9 (toluene–MeOH 70:30) was submitted to preparative TLC on polyamide (water–MeOH–methyl ethyl ketone–acetylacetone 13:3:3:1) followed by purification over Sephadex LH-20 column using MeOH as eluent to give compounds **3** and **4**.

The structures were established by chemical and spectral analysis, mainly FAB-MS (+), IR, UV, ^{1}H NMR, ^{13}C NMR, and NMR experiments (DEPT, COSY, HSQC, and HMBC). All these data were in good agreement with the respective literature data [6–11].

Compound 1. $C_{19}H_{22}O_6$, IR spectrum (KBr, ν, cm^{-1}): 1751 (C=O of γ-lactone), 1730 (C=O of ester), 3418 (OH). Mass spectrum (FAB$^+$, 70 eV), *m/z* : 369 $[M + Na]^+$, 347 $[MH]^+$.

^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm, J/Hz): 2.98 (1H, m, H-1α), 1.74 (1H, m, H-2α), 2.24 (1H, m, H-2β), 4.56 (1H, m, H-3α), 2.85 (1H, t, $J_{5\alpha-6\beta} = J_{5\alpha-1\alpha} = 10.3$, H-5α), 4.27 (1H, dd, $J_{6\beta-5\alpha} = 10.3$, $J_{6\beta-7\alpha} = 9.2$, H-6β), 3.20 (1H, m, H-7α), 5.14 (1H, m, H-8β), 2.72 (1H, dd, $J_{9\alpha-9\beta} = 14.6$, $J_{9\alpha-8\beta} = 5.1$, H-9α), 2.40 (1H, dd, $J_{9\beta-9\alpha} = 14.6$, $J_{9\beta-8\beta} = 3.7$, H-9β), 6.24 (1H, d, $J_{13\text{-}7\alpha} = 3.4$, H-13), 5.63 (1H, d, $J_{13'\text{-}7\alpha} = 3.0$, H-13′), 5.15 (1H, s, H-14), 4.94 (1H, s, H-14′), 5.49 (1H, s, H-15), 5.37 (1H, s, H-15′), 6.34 (1H, s, H-18), 5.97 (1H, s, H-18′), 4.39 (2H, s, H-19).

^{13}C NMR (62.9 MHz, $CDCl_3$, δ, ppm): 45.3 (C-1), 39.0 (C-2), 73.7 (C-3), 152.1 (C-4), 51.5 (C-5), 78.4 (C-6), 47.6 (C-7), 74.3 (C-8), 37.0 (C-9), 141.7 (C-10), 137.3 (C-11), 169.1 (C-12), 122.7 (C-13), 118.1 (C-14), 113.8 (C-15), 165.3 (C-16), 139.2 (C-17), 126.7 (C-18), 62.2 (C-19).

This compound was identified as cynaropicrin [6, 7].

Compound 2. $C_{15}H_{10}O_5$, mp 349°C. UV (MeOH, λ_{max}, nm): 266, 330; +NaOH: 274, 339, 390; +$AlCl_3$: 269, 299, 343, 379; +$AlCl_3$/HCl: 269, 299, 342, 376; +NaOAc: 268, 298, 338; +NaOAc/H_3BO_3: 268, 333.

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^{1}H NMR (250 MHz, MeOH-d_4, δ, ppm, J/Hz): 7.76 (2H, d, J = 8.5, H-2′, H-6′), 6.86 (2H, d, J = 8.5, H-3′, H-5′), 6.52 (1H, s, H-3), 6.40 (1H, d, J = 2.1, H-8), 6.12 (1H, d, J = 2.1, H-6).

This compound was characterized as 5,7,4′-trihydroxyflavone (apigenin) [8, 9].

Compound 3. $C_{15}H_{10}O_6$, mp 330°C. UV (MeOH, λ_{max}, nm): 253, 268, 349; +NaOH: 273, 406; +$AlCl_3$: 273, 419; +$AlCl_3$/HCl: 262, 279, 295, 359, 387; +NaOAc: 265, 349; +NaOAc/H_3BO_3: 258, 372.

^{1}H NMR (250 MHz, MeOH-d_4, δ, ppm, J/Hz): 7.35 (2H, m, H-2′, H-6′), 6.90 (1H, d, J = 8.5, H-5′), 6.53 (1H, d, J = 2.0, H-8), 6.42 (1H, s, H-3), 6.15 (1H, d, J = 2.0, H-6).

This compound was characterized as 5,7,3′,4′-tetrahydroxyflavone (luteolin) [8, 10].

Compound 4. $C_{22}H_{22}O_{12}$, UV (MeOH, λ_{max}, nm): 285, 348; +NaOH: 294, 387; +$AlCl_3$: 276, 302, 388; +$AlCl_3$/HCl: 284, 317, 384; +NaOAc: 287, 347; +NaOAc/H_3BO_3: 248, 344.

^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm, J/Hz): 8.13 (1H, d, J = 2.0, H-2′), 7.97 (1H, dd, J = 8.5, 2.0, H-6′), 7.10 (1H, d, J = 8.5, H-5′), 6.95 (1H, d, J = 2.0, H-8), 6.60 (1H, J = 2.0, H-6), 5.17 (1H, d, J = 7.6, H-1″ glucose), 4.00–3.20 (sugar protons), 4.13 (3H, s, O-CH_3).

Acid hydrolysis of this compound produced isorhamnetin and glucose. This compound was characterized as isorhamnetin 4′-glucoside [8, 11].

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