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FLAVONOIDS OF *Serratula cichoracea* AND THEIR ANTIOXIDANT ACTIVITY

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Numerous studies have showed that the genus *Serratula* is widely used in traditional medicine [1–3]. In our effort to find active compounds from medicinal Algerian species, we report herein our search concerning the antioxidant effect of the ethyl acetate extract of flowers of *S. cichoracea* using DPPH test and the isolation of its secondary metabolites. This species has not been previously investigated.

Serratula cichoracea was collected during the flowering phase in June 2002, in the East of Algeria, and was authenticated by Dr. D. Sarri (Biology Department, University of M'Sila, Algeria) on the basis of Quezel and Santa [4]. A voucher specimen was deposited in the Herbarium of the Department of Nature and Life Sciences, Mentouri University, Constantine (CSC01/06/02).

Dried flowers (2208 g) of *S. cichoracea* were macerated with EtOH-H_2O (80:20 v/v) for 24 hours three times. The crude extract was concentrated at room temperature and diluted with 500 mL H_2O. After filtration, the remaining aqueous solution was extracted successively with petroleum ether, $CHCl_3$, EtOAc, and *n*-BuOH. The organic layers were dried with Na_2SO_4 giving, after removal of solvents under reduced pressure, petroleum ether (0.16 g), $CHCl_3$ (5.90 g), EtOAc (19.15 g), and *n*-BuOH (26.4 g) extracts.

The ethyl acetate extract of the flowers of *S. cichoracea* was examined for *in vitro* antioxidant properties using DPPH test. The results showed that this extract had significant antioxidant activity, exhibiting an IC_{50} of 5.52 μg/mL. On the basis of this result, the extract was chromatographed on a 230–400 mesh silica gel column eluted with a gradient of chloroform/acetone to yield 14 fractions from which five compounds were isolated and purified by preparative TLC on silica gel using *n*-hexane/EtOAc and petroleum ether/cyclohexane/acetone as elution systems. The structures were elucidated by UV and ^{1}H NMR analysis. All these data were in good agreement with the respective literature data [5–7].

Compound 1: $C_{16}H_{12}O_7$, mp. 276°C; UV (MeOH, λ_{max}, nm): 256, 355; +NaOH: 271, 322, 404; +$AlCl_3$: 275, 425; +$AlCl_3$/HCl: 268, 296, 358, 396; +NaOAc: 273, 318, 391; +NaOAc/H_3BO_3: 263, 380.

^{1}H NMR (250 MHz, CD_3OD, δ, ppm, J/Hz): 7.51 (1H, d, J = 2.5, H-2′), 7.42 (1H, dd, J = 8.1, J = 2.5, H-6′), 6.79 (1H, d, J = 8.1, H-5′), 6.26 (1H, d, J = 2.1, H-8), 6.13 (1H, d, J = 2.1, H-6), 3.64 (3H, s, 3-OMe).

This compound was identified as 5,7,3′,4′-tetrahydroxy-3-methoxyflavone (3-methylquercetin).

Compound 2: $C_{15}H_{10}O_5$, mp 349°C; UV (MeOH, λ_{max}, nm): 266, 330; +NaOH: 275, 324, 390; +$AlCl_3$: 277, 301, 341, 387; +$AlCl_3$/HCl: 277, 301, 341, 387; +NaOAc: 278, 300, 380; +NaOAc/H_3BO_3: 273, 279, 350.

^{1}H NMR (250 MHz, CD_3OD, δ, ppm, J/Hz): 7.78 (2H, d, J = 8.9, H-2′, H-6′), 6.90 (2H, d, J = 8.9, H-3′, H-5′), 6.51 (1H, s, H-3), 6.42 (1H, d, J = 2.1, H-8), 6.22 (1H, d, J = 2.1, H-6).

This compound was characterized as: 5,7,4′-trihydroxyflavone (apigenin).

Compound 3: $C_{16}H_{12}O_5$, mp 262°C; UV (MeOH, λ_{max}, nm): 269, 347; +NaOH: 277, 321, 392; +$AlCl_3$: 276, 299, 343, 387; +$AlCl_3$/HCl: 281, 305, 342, 392; +NaOAc: 274, 304, 369; +NaOAc/H_3BO_3: 269, 347.

^{1}H NMR (250MHz, CD_3OD, δ, ppm, J/Hz): 7.86 (2H, d, J = 8.9, H-2′, H-6′), 6.95 (2H, d, J = 8.9, H-3′, H-5′), 6.57 (1H, s, H-3), 6.33 (1H, d, J = 2.0, H-8), 6.16 (1H, d, J = 2.0, H-6), 3.35 (3H, s, 4-OMe).

This compound was characterized as: 5,7-dihydroxy-4′-methoxyflavone (acacetin).

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Compound 4: $C_{15}H_{10}O_6$, mp 330°C; UV (MeOH, λ_{max}, nm): 255, 267, 349; +NaOH: 267, 328, 401; +$AlCl_3$: 273, 416; +$AlCl_3$/HCl: 264, 296, 356, 386; +NaOAc: 257, 368; +NaOAc/H_3BO_3: 267, 359.

^{1}H NMR (250MHz, CD_3OD, δ, ppm, J/Hz): 7.39 (2H, m, H-2′, H-6′), 6.92 (1H, d, J = 8.0, H-5′), 6.54 (1H, s, H-3), 6.44 (1H, d, J = 2.0, H-8), 6.21 (1H, d, J = 2.0, H-6).

This compound was characterized as: 5,7,3′,4′-tetrahydroxyflavone (luteolin).

Compound 5: $C_{16}H_{12}O_5$, mp 286°C; UV (MeOH, λ_{max}, nm): 268, 345; +NaOH: 274, 393; +$AlCl_3$: 276, 363, 382; +$AlCl_3$/HCl: 276, 299, 347, 382; +NaOAc: 271, 381; +NaOAc/H_3BO_3: 268, 342.

^{1}H NMR (250MHz, CD_3OD, δ, ppm, J/Hz): 7.84 (2H, d, J = 8.1, H-2′, H-6′), 6.90 (2H, d, J = 8.1, H-3′, H-5′), 6.61 (1H, s, H-3), 6.43 (1H, d, J = 2.1, H-8), 6.20 (1H, d, J = 2.1, H-6), 3.37 (3H, s, 7-OMe).

This compound was characterized as: 5,4′-dihydroxy-7-methoxyflavone (genkwanin).

Compound **1** (3-methylquercetin) was examined for *in vitro* antioxidant properties using the DPPH test under the same conditions as the extract, giving an IC_{50} of 3.52 μg/mL compared to that of quercetin, 3.49 μg/mL, which is used as control molecule.

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