PHENOLIC COMPOUNDS FROM *Centaurea africana*

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The genus *Centaurea* contains more than 700 species. It is represented by 45 in Algeria. As part of a systematic examination of the Algerian species, we have investigated *C. africana*, which is endemic to Algeria. This work concerns the phytochemical study of the ethyl acetate soluble part of the aqueous ethanol extract of the leaves and flowers.

Centaurea africana (Asteraceae) was collected during the flowering phase in May 2001, in the East of Algeria, and was authenticated by Pr. A. Kaabeche (Biology Department, University of Setif, Algeria). A voucher specimen was deposited in the Herbarium of the Department of Natural and Life Sciences, Mentouri University, Constantine (CCA0501).

Leaves and flowers of *Centaurea africana* were dried (1800 g) and macerated with EtOH–H_2O (80:20 v/v) for 48 h three times. After remove of chlorophyll, the remaining aqueous solution was extracted successively with $CHCl_3$, EtOAc, and *n*-BuOH resulting in chloroform (11 g), ethylacetate (18 g), and *n*-BuOH (100 g) extracts.

The ethylacetate extract of *C. africana* was chromatographed on a 230–400 mesh silica gel column eluted with a gradient of hexane–EtOAc–MeOH to yield 29 fractions from which six compounds were isolated and purified by preparative TLC on silica gel using CH_2Cl_2–acetone, hexane–EtOAc, and CH_2Cl_2–MeOH as elution systems. The structures were elucidated by UV, ^{1}H NMR, ^{13}C NMR, HSQC, HMBC, ROESY, and MS analysis. All these data were in good agreement with the literature data [1–8].

All these structures are reported for the first time from *C. africana.*

Compound 1: $C_{10}H_{12}O_3$, mp 138°C; ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 9.86 (1H, s, OH), 7.80 (2H, d, J = 8.5, H-3′, H-5′), 6.97 (2H, d, J = 8.5, H-2′, H-6′), 3.68 (3H, s, OCH_3), 2.71 (2H, t, J = 7.0, H-3), 2.64 (2H, t, J= 7.0, H-2).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 180 $[M]^+$ (0.51), 165 $[M-15]^+$ (100), 121 (96.6), 109 (17.5).

These spectral data led to the structure of methyl 3-(4-hydroxyphenyl)propanoate.

Compound 2: $C_9H_{10}O_4$, mp 128–129°C; ^{1}H NMR (400 MHz, CD_3COCD_3, δ, ppm, J/Hz): 7.42 (1H, br.s, H-2), 7.40 (1H, br.d, J = 8.2, H-6), 6.79 (1H, d, J = 8.2, H-5), 4.28 (2H, q, J = 7.1, CH_2), 1.35 (3H, t, J = 7.1, CH_3).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 182 $[M]^+$ (38.2), 167 $[M-15]^+$ (3.1), 154 (16.1), 137 $[M-45]^+$ (100), 109 (14.1). These spectral data led to the structure of ethyl 3,4-dihydroxybenzoate.

Compound 3: $C_{16}H_{12}O_6$, mp. 291°C; UV (λ_{max}, MeOH, nm): 276, 332; +NaOH: 276, 327, 395; +$AlCl_3$: 304, 359; +$AlCl_3$/HCl: 300, 356; +NaOAc: 297, 373; +NaOAc/H_3BO_3: 275, 339.

^{1}H NMR (300 MHz, CD_3OD, δ, ppm, J/Hz): 7.84 (2H, br.d, J = 8.6, H-2′, H-6′), 6.92 (2H, br.d, H-3′, H-5′), 6.55 (1H, s, H-3), 6.49 (1H, s, H-8), 3.86 (3H, s, 6-OMe).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 300 $[M]^+$ (100), 285 $[M-15]^+$ (62.5), 257 $[M-15-28]^+$ (54.7), 167 (13.1), 139 (15.2), 121 (9.7), 118 (12.6), 93 (3.2).

The aglycone was identified as 4′,5,7-trihydroxy-6-methoxyflavone (hispidulin) [7, 8].

Compound 4: $C_{18}H_{16}O_8$, mp 196°C; UV (λ_{max}, MeOH, nm): 257, 271, 350; +NaOH: 271, 304, 387; +$AlCl_3$: 268, 298, 373; +$AlCl_3$/HCl: 265, 279, 365; +NaOAc: 273, 321, 373; +NaOAc/H_3BO_3: 270, 355.

^{1}H NMR (400 MHz, CD_3COCD_3, δ, ppm, J/Hz): 7.52 (1H, br.d, J = 8.2, H-6′), 7.50 (1H, br.s, H-2′), 7.07 (1H, d, J = 8.2, H-5′), 6.50 (1H, s, H-8), 3.84 (3H, s, 4′-OMe), 3.76 (3H, s, 3-OMe), 3.73 (3H, s, 6-OMe); ^{13}C NMR (100 MHz, CD_3COCD_3) 56.1 (OMe-6), 60.2 (OMe-3), 60.4 (OMe-4′), 94.4 (C-8), 105.1 (C-10), 112.4 (C-5′), 115.4 (C-2′), 120.8 (C-6′),

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122.8 (C-1′), 131.6 (C-6), 138.1 (C-3), 146.8 (C-3′), 150.7 (C-4′), 152.0 (C-9), 152.8 (C-5), 155.7 (C-2), 157.9 (C-7), 178.6 (C-4).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 360 $[M]^+$ (100), 345 $[M-15]^+$ (76.2), 317 (42.2), 299 (24.6), 183 (2.4), 166 (7.2), 151 (14.9), 123 (2.4).

These assignments were completed on the basis of the results of HSQC, HMBC, and ROESY experiments. This compound is characterized as: 3′,5,7-trihydroxy-4′,3,6-trimethoxyflavone (centaureidin) [1, 2].

Compound 5: $C_{10}H_{10}O_4$, mp167°C; ^{1}H NMR (400MHz, CD_3COCD_3, δ, ppm, J/Hz): 7.59 (1H, d, J = 16, H-3), 7.33 (1H, br.s, H-2′), 7.13 (1H, br.d, J = 8.1, H-6′), 6.87 (1H, d, J = 8.1, H-5′), 6.37 (1H, d, J = 16, H-2), 3.92 (3H, s, 3′-OMe).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 194 $[M]^+$, 179 $[M-15]^+$, 161 $[M-15-18]^+$ (5.7), 149 $[M-44]^+$ (13.5), 133 (16.8), 123 (5.2), 105 (9.2), 91 (16.7), 77 (12.8), 71 (23.1).

Identified as (*E*)-3-(4′-hydroxy-3′-methoxyphenyl)acrylic acid or 5-hydroxyferulic acid [3].

Compound 6: $C_{16}H_{12}O_7$, mp 272°C; UV (λ_{max}, MeOH, nm): 351, 270; +NaOH: 270, 341, 406; +$AlCl_3$: 275, 304, 340, 425; +$AlCl_3$/HCl: 284, 338, 368; +NaOAc: 273, 324, 387; +NaOAc/H_3BO_3: 265, 374.

^{1}H NMR (250MHz, CD_3COCD_3, δ, ppm, J/Hz): 7.53 (1H, br.s, H-2′), 7.49 (1H, br.d, J = 8.2, H-6′), 7.02 (1H, d, J = 8.2, H-5′), 6.63 (1H, s, H-8), 6.61 (1H, s, H-3), 3.89 (3H, s, 6-OMe);

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 316 $[M]^+$ (100), 301 $[M-15]^+$ (57.6), 273 $[M-15-28]^+$ (43.3), 167 (11.3), 134 (10.4).

Identified as 3′,4′,5,7-tetrahydroxy-6-methoxyflavone (nepetin) [1, 5].

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