Chemistry of Natural Compounds, Vol. 48, No. 3, July, 2012 [Russian original No. 3, May–June, 2012]

COMPONENTS OF *Matricaria pubescens* FROM ALGERIAN SEPTENTRIONAL SAHARA

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UDC 547.972

The air-dried aerial parts (1200 g) of *Matricaria pubescens* (Desf.) Schultz, collected during flowering (April 2008) at Ghardaia (Algerian Septentrional Sahara), were macerated at room temperature in a methanol solution (70%). The extract was concentred under low pressure, diluted and filtered to remove chlorophyll, then successively extracted with petroleum ether, dichloromethane, ethyl acetate, and *n*-butanol.

The butanolic extract (10 g) was column chromatographed on polyamid SC6, eluted with toluene–methanol with increasing polarity. Whatman 3MM paper chromatography using 15% AcOH and BAW (*n*-BuOH–AcOH–H_2O, 4:1:5; upper phase) and TLC on polyamid DC6, eluted with H_2O–MeOH–methylethylketone–acetylacetone (13:3:3:1) followed by column flash chromatography over Sephadex LH-20 in MeOH, led to four pure flavonoids (**1–6**).

The dichloromethane extract (8 g) was column chromatographed on silica gel (35–70 μm), eluted with petroleum ether–ethyl acetate with increasing polarity and then with methanol.

The major fraction was chromatographed on a silica gel column (20–45 mm), eluted with cyclohexane–ethyl acetate with increasing polarity. Further, TLC using silica gel plates, eluted with cyclohexane–ethyl acetate, led to compounds **7–9**.

All compounds were identified by ^{1}H NMR, ^{13}C NMR, EI-MS, and UV analytical methods and acid hydrolysis.

Acid Hydrolysis. Compounds **4–6** were treated with 2M HCl at 100°C for 1 h. The hydrolysates were extracted with EtOAc, and the aglycones were identified by their UV spectra in methanol and by comparison of their R_f with authentic samples. Sugars were identified in the aqueous residue by comparison with authentic samples on silica gel TLC plates impregnated with 0.2 M NaH_2PO_4, solvent Me_2CO–H_2O (9:1), and revealed with aniline malonate.

Compound 1, $C_{15}H_{10}O_5$, mp 345°C, identified as apigenin [1].

Compound 2, $C_{15}H_{10}O_6$, mp 330°C, identified as luteolin [2].

Compound 3, $C_{15}H_{10}O_7$, yellow needles (acetone), mp >300°C, identified as quercetin [3].

Compound 4, $C_{21}H_{20}O_{10}$, mp 220–222°C, identified as apigenin 7-*O*-glucoside [4].

Compound 5, $C_{21}H_{20}O_{11}$, mp 239–242°C, identified as luteolin 7-*O*-glucoside [5].

Compound 6, mp 218–212°C, identified as quercetin 3-*O*-glucoside [6].

Compound 7, $C_{10}H_8O_3$, mp 115–117°C (diethyl ether). UV spectrum (MeOH, λ_{max}, nm, log ε): 203.4 (1.332), 204 (1.903), 214 (1.191), 322 (1.162). IR (KBr, ν_{max}, cm^{-1}): 1707 (CO), 2840 (OCH_3), 1613 (aromatic ring). PMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.65 (1H, d, J = 10, H-4), 7.35 (1H, d, J = 10, H-5), 6.85 (1H, d, J = 2, H-6), 6.75 (1H, dd, J = 8 and 2, H-8), 6.25 (1H, d, J = 10, H-3), 3.85 (3H, s, OCH_3). ^{13}C NMR (500 MHz, $CDCl_3$, δ, ppm): 161.1 (C-2), 113.1 (C-3), 143.4 (C-4), 128.7 (C-5), 112.6 (C-6), 162.8 (C-7), 100.9 (C-8), 155.9 (C-9), 11.5 (C-10), 55.7 (OCH_3). Mass spectrum (DiC, NH_3), *m/z* 177 $[M - H]^+$. Characterized as herniarin [7].

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 0009-3130/12/4803-0470

Compound 8, $C_{10}H_{10}O_3$, mp 115–117°C (diethyl ether). UV spectrum (MeOH, λ_{max}, nm, log ε): 204.4 (1.189), 279.7 (0.107). IR (KBr, ν_{max}, cm^{-1}): 1752 (CO), 2850 (OCH_3), 1652 (aromatic ring). PMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz), 7.06 (1H, d, J = 8, H-5), 6.66 (2H, dd, J = 8 and 2, H-6), 6.02 (1H.d, J = 2, H-8), 4.28 (2H, dd, J = 14 and 6, H-4), 4.18 (2H, dd, J = 14 and 6, H-3), 3.75 (3H, s, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 146.1 (C-2), 40.3 (C-3), 36.9 (C-4), 151.4 (C-5), 111.6 (C-6), 160.5 (C-7), 120.2 (C-8), 129.4 (C-9), 108.8 (C-10), 55.4 (OCH_3). Mass spectrum (DiC, NH_3), *m/z* 179 $[M - H]^+$. Characterized as 3,4-dehydroherniarin [7].

Compound 9, $C_{14}H_{19}NOS$, mp 104–106°C. PMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.25 (1H, dd, J = 15 and 8, H-3), 7.17 (1H, d, J = 5, H-5′ thienyl), 6.95 (1H, dd, J = 5 and 3.5, H-4′ thienyl), 6.81 (1H, d, J = 3.5, H-3′ thienyl), 6.22 (2H, m, H-4 and H-5), 5.82 (1H, d, J = 15, H-2), 5.61 (3H, t, J = 6.5, NH), 3.69 (2H, d, J = 5, CH_2), 3.18 (2H, dd, J = 7 and 6.5, $NHCH_2CH$), 1.81 (1H, nonat, J = 7, $CHMe_2$), 0.93 (6H, d, J = 6.5, $2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 166.2 (C-1), 141.6 (C-2′ thienyl), 140.2 (C-3), 139.1 (C-5), 129.6 (C-4), 127.0 (C-4′ thienyl), 125.0 (C-3′ thienyl), 124.0 (C-5′ thienyl), 123.5 (C-2), 47.0 (N-CH_2), 33.1 (C-6), 29.6 (C-isobutyl), 20.1 (2Me). Mass spectrum (DiC/NH_3), *m/z* 250 $[M - H]^+$ and 177, 149 corresponding to the loss of $NHCH_2Me_2$ then CO, respectively. Characterized as (2*E*,4*E*)-6-(2-thienyl)-2,4-hexadiene-isobutylamide [8].

ACKNOWLEDGMENT

The authors thank the (DG/RSDT, MESRS), Algeria for financial support.

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