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FLAVONOIDS FROM *Physospermum acteaefolium*

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The genus *Physospermum* (Apiaceae) comprises some 16 species. Cytotoxic triterpene saponins have recently been isolated from the roots of *Physospermum verticillatum*, the single reported species [1]. Two *Physospermum* species, *P. acteaefolium* Presl. and *P. cornubiense,* which is used to flavor sweet foods, grow in Algeria [2].

The aerial parts of *Physospermum acteaefolium* Presl. were collected on May 2008 in the region of the Babors Mountains [2]. A voucher specimen was deposited in the Herbarium of the Laboratory of Therapeutic Substances (LOST) at Mentouri University (LOST.Pa.05.06).

Air-dried and powdered aerial parts (800 g) of *Physospermum acteaefolium* were extracted with 70% MeOH. The residue was dissolved in boiling water and extracted with ethyl acetate and *n*-BuOH, successively. The butanolic extract 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–metylethylketone–acetylacetone (13:3:3:1), followed by column flash chromatography over Sephadex LH-20 in MeOH, led to seven compounds **1–7**, which were identified using UV, ^{1}H NMR, ^{13}C NMR, and MS analysis [3, 4].

Acid Hydrolysis. The pure compounds were treated with 2 M 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 impregnated with 0.2 M NaH_2PO_4, solvent Me_2CO–H_2O (9:1), revealed with aniline malonate.

Compound 1. $C_{15}H_{10}O_6$, yellow powder (acetone), mp 278–279°C. UV (MeOH, λ_{max}, nm): 266, 322 sh, 366. Characterized as kaempferol [3, 4].

Compound 2. $C_{15}H_{10}O_7$, yellow needles (acetone), mp >300°C. UV (MeOH, λ_{max}, nm): 375, 265. Characterized as quercetin [3, 4].

Compound 3. $C_{21}H_{20}O_{10}$, mp 232–233°C. UV (MeOH, λ_{max}, nm): 370, 258. Characterized as kaempferol 7-*O*-rhamnoside [3–5].

Compound 4. $C_{21}H_{20}O_{11}$, yellow crystals, mp 184–185°C. UV (MeOH, λ_{max}, nm): 350, 256. Characterized as quercetin 7-*O*-rhamnoside [3, 4, 6].

Compound 5. $C_{27}H_{30}O_{14}$, yellow amorphous powder, mp > 300°C. UV (MeOH, λ_{max}, nm): 263, 343; + NaOAc: 263, 393; + NaOAc/H_3BO_3: 265, 345; + $AlCl_3$: 277, 295 (sh), 345; + $AlCl_3$/HCl: 270, 290 (sh), 340, 393; + NaOMe: 271, 399 (increase in intensity). Positive FAB-MS *m/z* 579 $[M + 1]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.47 (d, J = 2.1, H-6), 6.84 (d, J = 2.1, H-8), 7.83 (d, J = 9.1, H-2′, H-6′), 6.97 (d, J = 9.1, H-3′, H-5′), 5.56 (d, J = 2.1, H-1″ Rha-1), 5.31 (d, J = 2.1, H-1‴ Rha-2), 3.05–3.92 (sugar protons), 1.16 (d, J = 6.3, CH_3-Rha-1), 0.83 (d, J = 6.4, CH_3-Rha-2). Acid hydrolysis of **5** gave kaempferol and L-rhamnose. Compound **6** was identified as kaempferol 3,7-dirhamnoside [5].

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Compound 6. $C_{27}H_{30}O_{17}$, yellow amorphous powder, mp 197–199°C. UV (MeOH, λ_{max}, nm): 268, 348; + NaOH: 276, 402; + $AlCl_3$: 273, 328, 425; + $AlCl_3$/HCl: 275, 295, 353, 387; + NaOAc: 269, 350, 407. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.51 (1H, dd, J = 8.5, 2.0, H-6′), 7.47 (1H, d, J = 2.0, H-2′), 6.83 (1H, d, J = 8.5, H-5′), 6.84 (1H, s, H-8), 6.62 (3H, s, H-6), 4.84 (1H, d, J = 8.2, H-1″), 4.66 (1H, d, J = 7.8, H-1‴), 3.05–3.90 (sugar protons). Acid hydrolysis of **6** gave quercetin and D-glucose. Compound **6** was identified as quercetin 3,7-diglucoside [7].

Compound 7. $C_{33}O_{20}H_{40}$, yellow needles, mp 226–228°C. UV (MeOH, λ_{max}, nm): 245 sh, 266, 318 sh, 352; + $AlC1_3$: 256 sh, 275, 302, 356, 400; + $AlCl_3$/HC1): 275, 300 sh, 350, 400; + NaOMe: 245, 270, 300 sh, 350 sh, 390; + NaOAc: 267, 320 sh, 360, 405 sh; + NaOAc/H_3BO_3: 266, 320 sh, 353. Positive FAB-MS: *m/z* 779 $[M + Na]^+$, 757 $[M + H]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.42 (1H, d, J = 1.8, H-6), 6.75 (1H, d, J = 1.8, H-8), 8.15 (2H, d, J = 8.9, H-2′, H-6′), 6.85 (2H, d, J = 8.9, H-3′, H-5′), 5.70 (1H, d, J = 7.5, H-1″ Gal), 5.20 (1H, d, J = 6.8, H-1‴ Rha), 5.15 (1H, d, J = 7.8, H-1⁗ Glc), 3.10–3.90 (sugar protons), 0.82 (d, J = 6.5, CH_3-Rha).

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 156.4 (C-2), 134.4 (C-3), 178.1 (C-4), 161.4 (C-5), 100.0 (C-6), 161.8 (C-7), 95.1 (C-8), 156.4 (C-9), 105.1 (C-10), 120.9 (C-1′), 131.3 (C-2′, C-6′), 115.8 (C-3′, C-5′), 161.7 (C-4′), 99.1 (C-1″ Gal), 77.1 (C-2″ Gal), 76.7 (C-3″ Gal), 68.4 (C-4″ Gal), 78.1 (C-5″ Gal), 60.5 (C-6″ Gal), 101.4 (C-1‴ Rha), 71.8 (C-2‴ Rha), 71.7 (C-3‴ Rha), 72.7 (C-4‴ Rha), 69.9 (C-5‴ Rha), 18.2 (CH_3 Rha), 100.1 (C-1⁗ Glc), 73.8 (C-2⁗ Glc), 78.9 (C-3⁗ Glc), 71.1 (C-4⁗ Glc), 77.5 (C-5⁗ Glc), 61.2 (C-6⁗ Glc) [8]. Acid hydrolysis of **7** gave kaempferol, D-galactose, L-rhamnose, and D-glucose. Compound **7** was identified as kaempferol-3-*O*-*β*-D-glucosyl(1→2)-*β*-D-galactoside 7-*O*-*α*-L-rhamnoside [8].

Compounds **1–7** are reported for the first time from the genus *Physospermum*. Compound **7** is reported for the second time from a natural source.

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