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BIOLOGICALLY ACTIVE COMPOUNDS FROM *Lepidium campestre* AND PULP FROM LEMON-JUICE PRODUCTION

D. Yu. Yusifova,[1] I. S. Movsumov,[1] E. A. Garaev,[1]* V. Mahiou-Leddet,[2] F. Mabrouki,[2] G. Herbette,[3] B. Baghdikian,[2] and E. Ollivier[2]

In continuation of the search for possible new sources of biologically active compounds, we studied the aerial parts of *Lepidium campestre* (L.) W.T.Aiton of the family Cruciferae Juss. that was growing in Azerbaijan [1] and fruit of *Citrus limon* Burm. of the family Rutaceae Juss. [2, 3].

Aerial parts of *L. campestre* were collected during full flowering in the middle of July 2012 in the vicinity of Kubinsky District, Azerbaijan Republic. Pulp was produced during lemon-juice production at facilities in Lenkaransky Districts in autumn 2014. Air-dried ground aerial parts (1.0 kg) of *L. campestre* were extracted with EtOH (95%). The extracts were evaporated to 150–200 mL, diluted with H_2O (150 mL), and evaporated to an aqueous residue that was worked up sequentially with $CHCl_3$, EtOAc:hexane, and EtOAc.

The EtOAc–hexane extract afforded compound **1**, $C_{15}H_{10}O_6$, mp 275–277°C (EtOH), tetraacetate mp 182–184°C ($CHCl_3$–MeOH).

Kaempferol (3,5,7,4′-tetrahydroxyflavone) (1). ^{1}H NMR spectrum (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.18 (1H, d, H-6), 6.39 (1H, d, H-8), 8.08 (1H, d, H-2′), 6.90 (2H, d, H-3′, 5′), 8.08 (1H, d, H-6′). ^{13}C NMR spectrum (150 MHz, DMSO-d_6, δ, ppm): 148.1 (C-2), 137.1 (C-3), 177.4 (C-4), 162.5 (C-5), 99.3 (C-6), 165.6 (C-7), 94.5 (C-8), 158.3 (C-9), 104.5 (C-10), 123.7 (C-1′), 130.7 (C-2′), 116.2 (C-3′), 160.0 (C-4′), 116.2 (C-5′), 130.7 (C-6′) [4].

Compound **2** was isolated from the EtOAc extract and was a flavonoid [5] of formula $C_{26}H_{28}O_{14}$, mp 210–212°C (EtOH). Acid hydrolysis cleaved **2** into kaempferol (48%), L-arabinose, and L-rhamnose. The attachment site of the sugars to the aglycon was determined as before [6]. Alkaline hydrolysis of **2** (aqueous KOH solution, 0.5%, 2 h) produced kaempferol-3-*O*-α-L-arabinopyranoside (juglanin) of formula $C_{20}H_{18}O_{10}$, mp 224–226°C (EtOH). UV spectrum (MeOH, λ_{max}, nm): 266, 350. Stepwise acid hydrolysis (15% AcOH, 2 h) of **2** produced the intermediate monoglycoside kaempferol-7-*O*-α-L-rhamnopyranoside (rhamnoisorobinin) of formula $C_{21}H_{20}O_{10}$, mp 170–173°C (EtOH).

Kaempferol-3-*O*-α-L-arabinopyranoside-7-*O*-α-L-rhamnopyranoside (2). ^{1}H NMR spectrum (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.45 (1H, d, J = 2.2, H-6), 6.83 (1H, d, J = 2.2, H-8), 8.12 (1H, d, J = 8.8, H-2′, 6′), 6.9 (1H, d, J = 8.8, H-3′, 5′), 5.35 (1H, d, J = 5.5, H-1″), 3.75 (1H, dd, J = 6.9, 5.5, H-2″), 3.53 (1H, dd, J = 6.9, 3.0, H-3″), 3.66 (1H, m, H-4″), 3.58 (2H, dd, J = 11.6, 5.5, H-5″), 3.22 (2H, dd, J = 11.6, 2.2, H-5″), 5.56 (1H, d, J = 1.7, H-1‴), 3.85 (1H, br.s, H-2‴), 3.64 (1H, dd, J = 9.4, 3.3, H-3‴), 3.30 (1H, br.t, J = 9.4, H-4‴), 3.43 (1H, dq, J = 9.4, 6.2, H-5‴), 1.12 (3H, d, J = 6.1, H-6‴). ^{13}C NMR spectrum (150 MHz, DMSO-d_6, δ, ppm): 160.2 (C-2), 133.9 (C-3), 177.7 (C-4), 160.9 (C-5), 99.4 (C-6), 161.6 (C-7), 94.6 (C-8), 155.9 (C-9), 105.6 (C-10), 120.6 (C-1′), 131.1 (C-2′, 6′), 115.3 (C-3′, 5′), 156.8 (C-4′), 101.2 (C-1″), 70.8 (C-2″), 71.5 (C-3″), 66.0 (C-4″), 64.2 (C-5″), 98.4 (C-1‴), 69.8 (C-2‴), 70.1 (C-3‴), 71.6 (C-4‴), 69.8 (C-5‴), 17.9 (C-6‴) [7].

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1) Azerbaijan Medical University, Ul. Bakikhanova, 21, Baku, AZ 1022, Azerbaijan, e-mail: eldargar@mail.ru; 2) UMR-MD3, Laboratoire de Pharmacognosie et Ethnopharmacologie, Faculte′ de Pharmacie, Aix-Marseille Universite, 27 Boulevard Sean Monlin, CS 30064, 13385 Marseille Cedex 5, France; 3) Spectropole, FR 1739, Aix-Marseille Universite′ Campus Scientitique Saint Jerome, Servise 511, 13397 Marseille Cedex 20, France, e-mail: gaetan.herbette@univ-amu.fr.
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Compound **3**, ursolic acid, was isolated from freshly obtained lemon pulp (~1.0 kg). The EtOAc extract of this same raw material produced yellow crystals of **4** [5].

***R*,*S*-Isomers of hesperidin (1:1) (4)**, mp 250–254°C (dec.); $[\alpha]_D^{20}$ –76° (*c* 2.0, Py), $C_{28}H_{34}O_{15}$. ^{1}H NMR spectrum (600 MHz, CD_3OD, δ, ppm, J/Hz): 5.41 (1H, dd, J = 12.4, 3.1, H-2), 3.13 (2H, dd, J = 17.2, 12.5, H-3), 2.80 (2H, dd, J = 17.2, 3.1, H-3), 6.20 (1H, d, J = 2.3, H-6), 6.19 (1H, d, J = 2.3, H-8), 6.97 (1H, d, J = 1.7, H-2′), 6.95 (1H, d, J = 8.2, H-5′), 6.93 (2H, dd, J = 8.5, 2.0, H-6′), 3.87 (3H, s, OCH_3), 4.94 (1H, d, J = 7.4, Glc H-1″), 3.44 (1H, dd, J = 9.7, 7.4, Glc H-2″), 3.45 (1H, t, J = 9.7, Glc H-3″), 3.36 (1H, br.t, J = 9.2, Glc H-4″), 3.59 (1H, m, Glc H-5″), 4.00 (2H, dd, J = 10.7, 1.5, Glc H-6″), 3.61 (2H, m, Glc), 4.69 (1H, d, J = 1.7, Rha H-1‴), 3.88 (1H, dd, J = 3.5, 1.7, Rha H-2‴), 3.68 (1H, dd, J = 9.6, 3.5, Rha H-3‴), 3.33 (1H, br.t, J = 9.7, Rha H-4‴), 3.62 (1H, m, Rha H-5‴), 1.19 (3H, d, J = 6.3, Rha H-6‴). ^{13}C NMR spectrum (150 MHz, CD_3OD, δ, ppm): 80.4 (C-2), 44.1 (C-3), 198.3 (C-4), 165.0 (C-5), 98.0 (C-6), 166.9 (C-7), 97.1 (C-8), 164.4 (C-9), 105.0 (C-10), 132.9 (C-1′), 114.7 (C-2′), 147.8 (C-3′), 149.4 (C-4′), 112.6 (C-5′), 119.1 (C-6′), 56.4 (OCH_3), 101.2 (C-1″), 74.4 (C-2″), 77.9 (C-3″), 71.3 (C-4″), 77.2 (C-5″), 67.4 (C-6″), 102.2 (C-1‴), 72.1 (C-2‴), 72.4 (C-3‴), 74.1 (C-4‴), 69.8 (C-5‴), 17.9 (C-6‴).

Thus, kaempferol-3-*O*-*α*-L-arabinopyranoside-7-*O*-*α*-L-rhamnopyranoside was isolated for the first time from plants of the genus *Lepidium* [8–12]. Lemon pulp from juice production yielded ursolic acid and a mixture of hesperidin *R*,*S*-isomers (1:1).

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