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# ACYLATED KAEMPFEROL DIGLYCOSIDE FROM *Allium senescens*

**I. Yu. Selyutina,[1] L. M. Tankhaeva,[2] and D. N. Olennikov[2*]**

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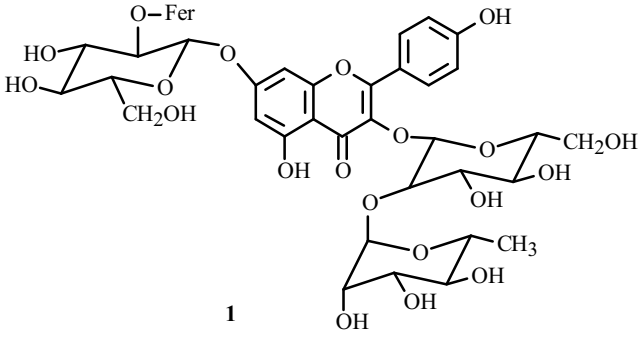
*Allium senescens* L. s. str. (Liliaceae) is a medicinal plant used in Tibetan medicine for treating diseases of the hematopoietic system [1]. The chemical composition of this species has been insufficiently studied. It is known to contain ascorbic acid [2], the alkaloid alliin [3], and two spirostanol glycosides gracillin and rhamnosidodioscin [4]. The goal of our work was to investigate flavonoids from the aerial part of *A. senescens*.

Preliminary investigations of the aerial part of *A. senescens* found flavonoids. Hydrolysis by HCl (2 M, 2 h, 100°C) of the total alcohol extract produced quercetin and kaempferol (HPTLC, solvent system 1; HPLC, conditions A).

Flavonoids were isolated by extracting raw material (aerial part of *A. senescens* collected near Ulan-Ude, Buryatiya, 2006; 1 kg) with ethanol (70%, 1:10). The alcohol extract was concentrated to an aqueous residue that was extracted successively with $CHCl_3$, ethylacetate, and *n*-butanol.

The butanol fraction (19 g) was chromatographed over a column of polyamide (Woelm for CC) using $H_2O \rightarrow$5-95% ethanol (HPTLC monitoring, solvent system 1). Fractions obtained by elution with ethanol (20%) (176 mg) were rechromatographed over silica gel (Chemapol, Silicagel L 100/400) using benzene:methanol (100:0→0:100) and then were separated by preparative HPLC (conditions B) to afford 35 mg of **1**, the purity of which was confirmed by HPLC (conditions A). Based on spectral data (UV, PMR, and $^{13}C$ NMR) and chemical transformations, **1** was identified as kaempferol-3-*O*-*β*-neohesperidoside-7-*O*-[2-*O*-(*trans*-feruloyl)]-*β*-D-glucopyranoside.




**1**

**Kaempferol-3-*O*-*β*-neohesperidoside-7-*O*-[2-*O*-(*trans*-feruloyl)]-*β*-D-glucopyranoside.** UV (MeOH, $\lambda_{max}$, nm): 253, 268 sh., 300, 320 sh., 355; +NaOH: 263, 269, 296, 370 sh., 395; +$AlCl_3$: 264, 295, 300, 322, 354, 391: +$AlCl_3$ + HCl: 267, 294, 299, 316, 354, 390; +AcONa: 269 sh., 299, 315, 360. Spectral ratios (HPLC, conditions A, $\lambda_1$, nm/$\lambda_2$, nm): 0.58 (280/360), 0.65 (300/360), 0.78 (320/360), 0.91 (340/360). Hydrolysis by HCl (2 M, 2 h) produced kaempferol and ferulic acid (HPTLC, solvent system 1) in addition to glucose and rhamnose in a 2:1 ratio (HPTLC/densitometry, solvent system 2). Table 1 lists the PMR spectrum (500 MHz, DMSO-$d_6$) and $^{13}C$ NMR spectrum (125.7 MHz, DMSO-$d_6$).

1) Central Siberian Botanical Garden, Siberian Branch, Russian Academy of Sciences, 630090, Novosibirsk-90, ul. Zolotodolinskaya, 101, fax: (83832) 30 19 86, e-mail: inessa@csbg.nsc.ru; 2) Institute of General and Experimental Biology, Siberian Branch, Russian Academy of Sciences, 670047, Ulan-Ude, ul. Sakh′yanovoi, 6, fax: (83012) 43 30 34, e-mail: oldaniil@rambler.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 621-622, November-December, 2008. Original article submitted June 25, 2008.

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TABLE 1. PMR and $^{13}C$ NMR Spectra of **1**

| C atom | $\delta_H$ (ppm, J/Hz) | $\delta_C$ (ppm) | C atom | $\delta_H$ (ppm, J/Hz) | $\delta_C$ (ppm) |
|---|---|---|---|---|---|
| 2 | - | 159.01 s | Rha | | |
| 3 | - | 135.05 s | 1 | 5.18 br.s | 104.57 d |
| 4 | - | 178.90 s | 2 | 3.80 s | 72.38 d |
| 5 | - | 162.95 s | 3 | 4.00 s | 71.29 d |
| 6 | 6.40 (d, J = 2.5) | 101.03 d | 4 | 3.34 s | 75.00 d |
| 7 | - | 163.84 s | 5 | 4.10 s | 69.95 d |
| 8 | 6.80 (d, J = 2.5) | 95.65 d | 6 | 1.00 (d, J = 6.5) | 17.97 q |
| 9 | - | 158.08 s | 7-*O*-Glc | | |
| 10 | - | 106.20 s | 1 | 5.40 (d, J = 8.0) | 98.35 d |
| 1′ | - | 123.32 s | 2 | 5.15 m | 74.68 d |
| 2′ | 8.08 (d, J = 9.0) | 132.00 d | 3 | 3.78 (dd, J = 10.0, 10.0) | 72.38 d |
| 3′ | 6.90 (d, J = 9.0) | 116.32 d | 4 | 3.54 (dd, J = 10.0, 10.0) | 71.30 d |
| 4′ | - | 166.87 s | 5 | 3.69 (dd, J = 10.0, 7.0) | 78.31 d |
| 5′ | 6.90 (d, J = 9.0) | 16.32 d | 6 | 2.72 (AB, J = 12.0, 2.0) | 62.50 d |
| 6′ | 8.08 (d, J = 9.0) | 132.00 d | Fer | | |
| 3-*O*-Glc | | | 1 | - | 125.22 s |
| 1 | 5.63 (d, J = 7.0) | 100.72 d | 2 | 7.81 (d, J = 3.0) | 131.72 d |
| 2 | 3.69 (dd, J = 10.0, 7.0) | 80.54 d | 3 | 7.80 (d, J = 8.0) | 157.61 s |
| 3 | 3.56 (dd, J = 10.0, 7.0) | 78.22 d | 4 | - | 161.92 s |
| 4 | 3.30 (dd, J = 10.0, 7.0) | 72.14 d | 5 | 7.80 (d, J = 8.0) | 116.89 d |
| 5 | 3.22 (d, J = 6.0) | 77.89 d | 6 | 6.78 (dd, J = 8.0, 3.0) | 131.90 d |
| 6 | 3.60 (AB, J = 12.0, 6.0) | 62.53 t | 7 | 7.70 (d, J = 17.5) | 148.64 d |
| | | | 8 | 6.51 (d, J = 17.5) | 115.91 d |
| | | | 9 | - | 168.81 s |
| | | | $CH_3O$ | 3.84 s | 57.12 q |

HPTLC was performed on Sorbfil PTSKh-AF-V plates. Solvent systems were toluene:ethylacetate:HCOOH (1, 20:11:3) and *i*-PrOH:$CHCl_3$:$H_2O$ (2, 7:4:1). Chromatograms were developed twice to heights of 4 and 8 cm. Flavonoids in chromatograms were detected by $AlCl_3$ (5%); phenolic acids, by $NH_3$ vapor and UV; carbohydrates, by anilinium phthalate.

HPLC conditions: A, Milikhrom A-02 liquid chromatograph, Nucleosil C18 column (2 × 75 mm, 5 μm particle size), mobile phase TFA (0.1%) in $CH_3CN$, flow rate 150 μL/min, UV detector (λ = 220, 254, 360 nm); B, Waters 600E liquid chromatograph, Lichrospher RP-18 column (4.6 × 200 mm, 5 μm particle size), mobile phase $CH_3CN$ gradient in water 10%→50%, UV detector (λ = 310 nm).

The total content of flavonoids in the aerial part of *A. senescens* was 0.77% of the mass of air-dried raw material (differential spectrophotometry [5]). According to HPLC (conditions A), **1** was the main component of the phenolic compounds (0.11-0.19% of the air-dried mass of raw material).

Kaempferol-3-*O*-*β*-neohesperidoside-7-*O*-[2-*O*-(*trans*-feruloyl)]-*β*-D-glucopyranoside (**1**) was observed previously in the aerial part of *A. ursinum* [6] and *A. neapolitanum* [7] and was isolated for the first time from *A. senescens*.

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