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FLAVONOIDS FROM *Tanacetum vulgare* FLOWERS

A. V. Kurkina,[1]* A. I. Khusainova,[1]
E. D. Daeva,[2] and V. I. Kadentsev[2]

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Flowers of tansy (*Tanacetum vulgare* L.) are used in various medicinal forms as antihelminthic and cholegogic agents [1–5]. The pharmacological properties of tansy flower preparations are due mainly to the essential oil (thujone and other terpenoids) and flavonoids. According to various literature sources [3–5], apigenin, acacetin, luteolin, cinaroside, eupatilin, jaceidin, and jaceoside are the main flavonoids in tansy flowers. However, reports in the domestic and foreign literature are somewhat contradictory.

The goal of the present work was to study the flavonoid composition of tansy flowers growing in Samara Oblast (Russia).

We studied tansy flowers collected near Nizhnee Sancheleevo village, Samara Oblast (July, 2008). Flowers (150 g) were extracted exhaustively with EtOH (70%) by combining maceration (24 h) with subsequent thermal extraction at 85–90°C. The aqueous alcohol extracts were evaporated in vacuo to a thick residue (~50 mL). The condensed extract was dried over L 40/100 silica gel. The resulting powder (extract + silica gel) was placed on a layer of silica gel that was formed in $CHCl_3$ and eluted by $CHCl_3$ and $CHCl_3$:EtOH in various ratios (97:3, 95:5, 93:7, 90:10, 88:12, 85:15, 80:20, 70:30). The separation of the compounds was monitored by TLC on Silufol UV 254 and Sorbfil PTSKh-AF-A-UV plates using $CHCl_3$:EtOH (4:1) and $CHCl_3$:MeOH:H_2O (26:14:3).

Fractions containing the dominant compound **1** were combined. The precipitate that formed in these was separated and recrystallized from EtOH to afford **1** in 0.2% yield of the air-dried raw material mass. Fractions containing compounds **2**–**4** (each separately) were transferred to a chromatographic column (sorbent height 4.0 cm; diameter, 5 cm). The respective chromatographic column was eluted by H_2O and aqueous EtOH (20%, 40, 70, and 96). Purification over polyamide columns afforded **2** (96% EtOH eluent), **3** (40% EtOH eluent), and **4** (70% EtOH eluent). The compounds were purified additionally by recrystallization from aqueous EtOH.

The chemical structures of flavonoids **1**–**4** were elucidated using PMR and UV spectroscopy and mass spectrometry in addition to chemical transformations. Flavonoids **1** and **3** were cleaved by acid hydrolysis (10% HCl, 100°C, 2 h) and *β*-glucosidase (Fluka, Hungary) into glucose and the aglycons, which were identified by TLC as acacetin (5,7-dihydroxy-4′-methoxyflavone) (**2**) and apigenin (5,7,4′-trihydroxyflavone) (**4**), respectively. Flavonoids **2** and **4** were also isolated from tansy raw material in the free state. The PMR spectrum of **1** showed two 2H doublets at 8.07 and 7.14 ppm with SSCC (J) 9 Hz that were assigned to H-2′,6′ and H-3′,5′, respectively; two 1H doublets at 6.84 and 6.45 ppm with J = 2.5 Hz that were characteristic of ring A protons (H-8 and H-6), and a singlet for H-3 at 6.95 (flavone compound). A 3H singlet at 3.87 for the C-4′ OCH_3 group and a singlet for the 5-OH of the flavonoid were observed in the PMR spectrum. The carbohydrate was placed on the 7-OH group on the basis of these results and those from enzymatic hydrolysis, and UV spectroscopy (lack of a bathochromic shift of the short-wavelength absorption band in the presence of NaOAc) [6]. The glucose was bonded as *β*-D-glucopyranosyl (characteristic doublet for the anomeric proton at 5.35 ppm with J = 7.2 Hz).

The chemical studies and spectra data suggested that **1** had the structure 5,7-dihydroxy-4′-methoxyflavone 7-*O*-*β*-D-glucopyranoside (tilianin) [7].

The chemical structure of **3** was studied analogously. Based on UV, NMR, and mass spectral data in addition to results from chemical transformations it was identified as 5,7,4′-trihydroxyflavone 7-*O*-*β*-D-glucopyranoside (cosmosiin).

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1) Samara State Medical University, 443099, Samara, Russia, fax: 8 (846) 333 29 76, e-mail: Annushkae@yandex.ru; 2) N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, 119991, Moscow, e-mail: Lena_Daeva@mail.ru, vkadents@ioc.ac.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 256–257, March–April, 2011. Original article submitted July 19, 2010.

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Compounds **1** and **3** were isolated for the first time from tansy flowers. Tilianin (**1**) was the dominant flavonoid in this raw material. This is of interest from the viewpoint of standardization, especially for potential use in HPLC analytical procedures, keeping in mind that fact that the hepatoprotective and cholegogic preparation Tanatsekhol is produced from the total flavonoids in the Russian Federation [1, 3, 4].

PMR spectra were taken on Bruker AM 300 (300 MHz) and Gemini-200 (200 MHz) instruments; mass spectra, on a Kratos MS-30 mass spectrometer; UV spectra, on a Specord 40 spectrophotometer (Analytik Jena).

Tilianin (1), white crystals, $C_{22}H_{22}O_{10}$, aglycon $[M]^+$ 284 (100%), mp 236–239°C (aqueous EtOH). UV spectrum (EtOH, λ_{max}, nm): 270, 327; +NaOAc: 270, 327; +NaOMe: 290, 367; +$AlCl_3$: 279, 300, 336, 382; +$AlCl_3$ + HCl: 279, 300, 336, 382. PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.2–3.8 (6H, glucose), 3.87 (3H, s, OCH_3), 5.35 (1H, d, J = 7.2, glucopyranose H-1′′), 6.45 (1H, d, J = 2.5, H-6), 6.84 (1H, d, J = 2.5, H-8), 6.95 (1H, s, H-3), 7.14 (2H, d, J = 9, H-3′,5′), 8.07 (2H, d, J = 9, H-2′,6′), 12.92 (1H, s, 5-OH).

Acacetin (2), light-yellow crystals, $C_{16}H_{12}O_5$, mp 264–267°C (aqueous EtOH). UV spectrum (EtOH, λ_{max}, nm): 270, 328; +NaOAc: 275, 350sh; +NaOMe: 278, 374; +$AlCl_3$: 279, 300, 337, 382; +$AlCl_3$ + HCl: 279, 300, 337, 382. PMR spectrum (200 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.86 (3H, s, OCH_3), 6.43 (1H, d, J = 2, H-6), 6.80 (d, J = 2.5, H-8), 6.96 (1H, s, H-3), 7.16 (2H, d, J = 9, H-3′,5′), 8.08 (2H, d, J = 9, H-2′,6′), 12.90 (1H, s, 5-OH). Mass spectrum (70 eV, 200°C, *m/z*, %): 284 (100) $[M]^+$.

Cosmosiin (3), light-yellow crystals, $C_{21}H_{20}O_{10}$, aglycon $[M]^+$ 270 (100%), mp 225–227°C (aqueous EtOH). UV spectrum (EtOH, λ_{max}, nm): 270, 334; +NaOAc: 269, 378; +NaOMe: 278, 397; +$AlCl_3$: 279, 330, 347, 384; +$AlCl_3$ + HCl: 279, 330, 347, 384. PMR spectrum [200 MHz, $(CD_3)_2CO$, δ, ppm, J/Hz]: 3.3–4.0 (6H, glucose), 5.16 (1H, d, J = 7.2, glucopyranose H-1′′), 6.44 (1H, d, J = 2.5, H-6), 6.82 (1H, d, J = 2.5, H-8), 6.90 (1H, s, H-3), 7.03 (2H, d, J = 9, H-3′,5′), 7.96 (2H, d, J = 9, H-2′,6′), 12.52 (1H, s, 5-OH).

Apigenin (4), light-yellow crystals, $C_{15}H_{10}O_3$, mp 340–343°C (aqueous EtOH). UV spectrum (EtOH, λ_{max}, nm): 270, 335; +NaOAc: 276, 378; +NaOMe: 278, 397; +$AlCl_3$: 279, 330, 348, 385; +$AlCl_3$ + HCl: 279, 330, 348, 385. PMR spectrum [200 MHz, $(CD_3)_2CO$, δ, ppm, J/Hz]: 6.43 (1H, d, J = 2.5, H-6), 6.81 (1H, d, J = 2.5, H-8), 6.89 (1H, s, H-3), 7.02 (2H, d, J = 9, H-3′,5′), 7.95 (2H, d, J = 9, H-2′,6′), 12.50 (1H, s, 5-OH). Mass spectrum (70 eV, 200°C, *m/z*, %): 270 (100) $[M]^+$.

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