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FLAVONOL GLYCOSIDES FROM LEAVES OF *Allium microdictyon*

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The composition of flavonoids from leaves of Allium microdictyon *Prokh. (Amaryllidaceae) was studied for the first time and included 14 compounds including two new flavonol glycosides **1** and **2**. UV, IR, and NMR spectroscopic and mass spectrometric data determined that **1** was quercetin-3-*O*-(2″-O-α-L-rhamnopyranosyl)-β-D-glucopyranoside-7-O-β-D-glucuronopyranoside (quercetin-3-O-neohesperidoside-7-O-glucuronide). Compound **2** had the structure kaempferol-3-O-(2″-O-α-L-rhamnopyranosyl)-β-D-glucopyranoside-7-O-β-D-glucuronopyranoside (kaempferol-3-O-neohesperidoside-7-O-glucuronide).*

Keywords: *Allium microdictyon*, Amaryllidaceae, flavonol glycosides.

Leafy onions are called by the common name leeks and are widely used in European and Asian cuisines as a green seasoning with a distinct garlic aroma and specific taste. Known representatives of this onion group include species of the sections Ophioscordon (*Allium ursinum* L.) and Anguinum (*A. victorialis* L., *A. ochotense* Prokh., *A. microdictyon* Prokh.). The chemistry of species growing in European Russia, *A. ursinum* [1] and *A. victorialis* [2], and the Far-Eastern species *A. ochotense* [3] has previously been studied although *A. microdictyon* found in Siberia still remains an unstudied species. According to a spectrophotometric analysis, leaves of *A. microdictyon* accumulate flavonoids (2.90 ± 0.05/14.53 ± 0.31 mg/g recalculated for fresh/air-dried raw material), which is also characteristic of other *Allium* species [3–5]. The results indicated that the component composition of flavonoids from *A. microdictyon* should be studied so that became the goal of the present work.

Fresh leaves of *A. microdictyon* afforded EtOAc and BuOH fractions that were separated by column chromatography (CC) over polyamide, Sephadex LH-20, and RP-SiO_2 and by preparative HPLC to isolate two new flavonol glycosides **1** and **2** in addition to the known flavonoids astragalin (**3**) [4], isoquercitrin (**4**) [6], kaempferol-3-*O*-glucoside-7-*O*-glucuronide (**5**) [7], kaempferol-3-*O*-neohesperidoside (**6**) [4], kaempferol-3,7-di-*O*-glucoside (**7**) [4], quercetin-3-*O*-glucoside-7-*O*-glucuronide (**8**) [7], quercetin-3,7-di-*O*-glucoside (**9**) [8], isorhamnetin-3-*O*-(2″-*O*-rhamnosyl-6″-*O*-glucosyl)-glucoside (**10**) [5], kaempferol-3-*O*-neohesperidoside-7-*O*-glucoside (**11**) [4], quercetin-3-*O*-(2″-*O*-rhamnosyl-6″-*O*-glucosyl)-glucoside (**12**) [9], quercetin-3-*O*-neohesperidoside-7-*O*-glucoside (**13**) [10], and quercetin-3-*O*-gentiobioside-7-*O*-glucuronide (**14**) [7].

Compound **1** had molecular formula $C_{33}H_{38}O_{22}$ according to HR-ESI-MS (*m*/*z* 787.4271 $[M + H]^+$; calcd for $C_{33}H_{39}O_{22}$, 787.5990) and ^{13}C NMR spectroscopy. Total hydrolysis of **1** produced quercetin, D-glucose, L-rhamnose, and D-glucuronic acid. UV spectroscopy in the presence of ionizing additives was indicative of substituted C-3 and C-7 hydroxyls of the aglycon [7, 8].

Mass spectra (ESI-MS) in positive-ion mode showed the protonated ion (*m*/*z* 787) and ions due to sequential loss of rhamnose (*m*/*z* 641), glucose (*m*/*z* 479), and glucuronic acid (*m*/*z* 303). Enzymatic hydrolysis by β-glucosidase did not cause changes, which indicated that the glucose was not terminal. Formation of quercetin-3-*O*-glucoside-7-*O*-glucuronide (**8**) [7] was observed after incubation with α-rhamnosidase, suggesting the rhamnose may have been in a terminal position.

Oxidation by H_2O_2 in alkaline solution formed a disaccharide, the chromatographic mobility of which agreed with that of neohesperidose (2-*O*-rhamnosylglucose). Loss of glucuronic acid as a result of the reaction with β-glucuronidase formed quercetin-3-*O*-neohesperidoside (calendoflavobioside) [11], which was previously isolated from *Calendula officinalis* L. (Asteraceae) [12].

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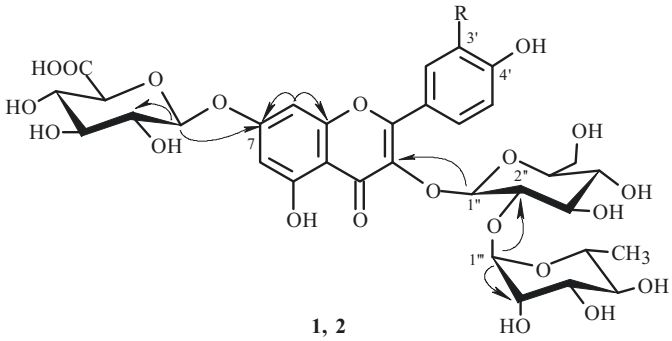
TABLE 1. PMR (500 MHz) and ^{13}C NMR Spectra (125 MHz) of **1** and **2** (MeOH-d_4, 298 K, δ, ppm, J/Hz) (*DMSO-d_6)

C atom	**1**		**2**	
	δ_H	δ_C	δ_H	δ_C
	Quercetin		Kaempferol	
2	–	157.3	–	156.8
3	–	133.1	–	133.3
4	–	177.8	–	177.1
5	–	160.2	–	160.4
6	6.43 (1H, d, J = 2.0)	99.0	6.46 (1H, d, J = 2.0)	99.2
7	–	162.7	–	162.4
8	6.75 (1H, d, J = 2.0)	94.5	6.81 (1H, d, J = 2.0)	94.7
9	–	156.0	–	156.3
10	–	105.2	–	105.0
1′	–	120.8	–	121.5
2′	7.93 (1H, d, J = 2.0)	115.0	8.11 (2H, d, J = 9.0)	130.4
3′	–	144.3	6.92 (2H, d, J = 9.0)	115.2
4′	–	148.9	–	159.0
5′	6.85 (1H, d, J = 9.0)	116.4	6.92 (2H, d, J = 9.0)	115.2
6′	7.52 (1H, dd, J = 2.0, 9.0)	121.7	8.11 (2H, d, J = 9.0)	130.4
5-OH	12.48 (1H, br.s)*		12.52 (1H, br.s)*	
3′-OH	9.57 (1H, br.s)*		–	
4′-OH	9.72 (1H, br.s)*		9.70 (1H, br.s)*	
	3-*O*-*β*-D-Glucopyranose			
1″	5.61 (1H, d, J = 7.1)	101.1	5.64 (1H, d, J = 7.0)	101.4
2″	3.98 (1H, m)	76.2	3.95 (1H, m)	76.3
3″	3.75 (1H, m)	77.9	3.79 (1H, m)	78.1
4″	3.45 (1H, m)	70.1	3.40 (1H, m)	70.3
5″	3.57 (1H, m)	77.5	3.52 (1H, m)	77.8
6″	3.87 (1H, dd, J = 2.0, 12.0, H_A), 3.61 (1H, m, H_B)	60.2	3.82 (1H, dd, J = 2.1, 12.0, H_A), 3.60 (1H, m, H_B)	60.1
	2″-*O*-*α*-L-Rhamnopyranose			
1‴	4.92 (1H, d, J = 1.8)	100.7	4.95 (1H, d, J = 2.1)	100.4
2‴	4.02 (1H, m)	70.4	3.99 (1H, m)	70.5
3‴	3.64 (1H, m)	70.9	3.65 (1H, m)	71.2
4‴	3.28 (1H, m)	72.4	3.21 (1H, m)	72.6
5‴	3.69 (1H, m)	68.4	3.71 (1H, m)	68.3
6‴	0.92 (3H, d, J = 6.2)	17.0	0.90 (3H, d, J = 6.0)	17.2
	7-*O*-*β*-D-Glucuronopyranose			
1⁗	5.14 (1H, d, J = 7.7)	99.4	5.11 (1H, d, J = 7.9)	99.7
2⁗	3.51 (1H, m)	73.0	3.47 (1H, m)	72.7
3⁗	3.40 (1H, m)	75.7	3.38 (1H, m)	75.9
4⁗	3.48 (1H, m)	71.2	3.42 (1H, m)	71.0
5⁗	4.10 (1H, d, J = 9.0)	75.4	4.06 (1H, d, J = 8.8)	75.3
6⁗	–	170.5	–	170.2

The PMR spectrum displayed a series of doublets characteristic of C-3 and C-7 substituted quercetin (δ_H 6.43–7.93) [8] and resonances for three anomeric protons at 5.61 (d, J = 7.1 Hz), 4.92 (d, J = 1.8 Hz), and 5.14 (d, J = 7.7 Hz) that were assigned to *β*-glucose, *α*-rhamnose, and *β*-glucuronic acid [7]. The resonance for the anomeric proton of the 3-*O*-glucose was shifted to weak field more strongly (δ_H 5.61) than the corresponding resonance in **8** (δ_H 5.31), which indicated that the neighboring C-2″ atom was substituted. This was confirmed by the location of the C-2″ resonance at weaker field (δ_C 76.2) than that in **8** (δ_C 74.2) in the ^{13}C NMR spectrum. Correlations between rhamnose proton H-1‴ (δ_H 4.92) and C-2″ in the HMBC spectrum confirmed that the glucose C-2″ hydroxyl was substituted by a rhamnose residue (Fig. 1). Additional correlations in the HMBC spectrum between glucose H-1″ (δ_H 5.61) and aglycon C-3 (δ_C 133.1) and between glucuronic acid H-1⁗ (δ_H 5.14) and aglycon C-7 (δ_C 162.7) were consistent with attachment of glucose and glucuronic acid at the quercetin C-3 and C-7 positions, respectively. Thus, the results showed that **1** was quercetin-3-*O*-(2″-*O*-*α*-L-rhamnopyranosyl)-*β*-D-glucopyranoside-7-*O*-*β*-D-glucuronopyranoside (quercetin-3-*O*-neohesperidoside-7-*O*-glucuronide).



1, 2

1: R = OH; **2:** R = H

Fig. 1. Structure and HMBC correlations in **1** and **2**.

The molecular formula of **2** was determined as $C_{33}H_{38}O_{21}$ (*m/z* 771.5742 $[M + H]^+$), calcd for $C_{33}H_{39}O_{21}$, 771.6000). Total hydrolysis formed kaempferol, D-glucose, L-rhamnose, and D-glucuronic acid. The PMR spectrum contained a series of doublets typical of kaempferol with substituted C-3 and C-7 (δ_H 6.46–8.11) [8]. UV spectroscopy with ionizing additives was also indicative of this. Enzymatic hydrolysis by β-glucosidase did not cause changes while α-rhamnosidase formed kaempferol-3-*O*-glucoside-7-*O*-glucuronide (**5**) [7]. Oxidative degradation by H_2O_2 produced neohesperidose. The reaction with β-glucuronidase gave kaempferol-3-*O*-neohesperidoside (**6**) [4]. Otherwise, mass spectrometric and NMR spectroscopic data were similar to those of **1**, indicating that **2** was a kaempferol derivative with the same set of carbohydrate residues and had the structure kaempferol-3-*O*-(2″-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside-7-*O*-β-D-glucuronopyranoside (quercetin-3-*O*-neohesperidoside-7-*O*-glucuronide).

3-*O*-Rutinoside-7-*O*-glucuronides of quercetin and kaempferol isomeric to **1** and **2** were observed earlier in flowers of *Tulipa gesneriana* L. (Liliaceae) [7]. Flavonol 3,7-di-*O*-glycosides were found in other leek species in the section Anguinum, *A. victorialis* L. [13] and *A. ochotense* Prokh. [3], which was probably their chemotaxonomic signature.

EXPERIMENTAL

Leaves of *A. microdictyon* were collected before flowering in Pribaikalsky District, Republic of Buryatia (May 28, 2019; 52°10′35.2182″ N, 107°42′14.7780″ E, 612 m above sea level; humidity 80.02 ± 2.62%). The species was determined by Dr. N. K. Chirikova (North-Eastern Federal University, Yakutsk, Russia). A specimen of the raw material is preserved in the herbarium of the IGEB, SB, RAS (No. BU/AMA-0519/12-19). The total flavonoid content in leaves of *A. microdictyon* was determined by spectrophotometry in the presence of $AlCl_3$ (recalculated as rutin) [14]. Column chromatography (CC) used polyamide, Sephadex LH-20, and reversed-phase silica gel (RP-SiO_2, Sigma-Aldrich, St. Louis, MO, USA). Spectrophotometric studies used an SF-2000 spectrophotometer (OKB Spectr, St. Petersburg, Russia). Mass spectrometric studies used an LCMS-8050 TQ-mass spectrometer (Shimadzu, Columbia, MD, USA) [15]. NMR spectra were recorded on a VXR 500S NMR spectrometer (Varian, Palo Alto, CA, USA). Preparative HPLC was performed on a Summit liquid chromatograph (Dionex, Sunnyvale, CA, USA) using a LiChrospher RP-18 column (250 × 10 mm, ∅ 10 μm; Supelco, Bellefonte, PA, USA); mobile phase H_2O (A) and MeCN (B); flow rate 0.8 mL/min; column temperature 26°C; and UV detection at λ 350 nm.

Extraction and Isolation of 1–14 from *A. microdictyon*. Fresh leaves (4.5 kg) were ground in a blender and extracted with EtOH (90%, 1:5) with heating (90°C) for 4 h. The EtOH extract was filtered and concentrated to dryness. The dry solid was suspended in H_2O (200 mL) and extracted with hexane, EtOAc, and BuOH to produce hexane (2.02 g), EtOAc (0.64 g), and BuOH fractions (3.62 g). The EtOAc fraction (0.6 g) was separated over polyamide (800 g) with elution by H_2O and EtOH (80%). The EtOH eluate was concentrated and chromatographed over Sephadex LH-20 (CC, 70 × 1 cm, EtOH–H_2O eluent, 90:10→0:100) and RP-SiO_2 (CC, 30 × 1 cm, H_2O–MeCN eluent, 70:30→50:50) and by prep. HPLC [gradient mode (%B): 0–90 min, 40–70%] to isolate seven compounds including astragalin (kaempferol-3-*O*-glucoside, 3 mg, **3**) [4], isoquercitrin (quercetin-3-*O*-glucoside, 6 mg, **4**) [6], kaempferol-3-*O*-glucoside-7-*O*-glucuronide (21 mg, **5**) [7], kaempferol-3-*O*-neohesperidoside (9 mg, **6**) [4], kaempferol-3,7-di-*O*-glucoside (52 mg, **7**) [4], quercetin-3-*O*-glucoside-7-*O*-glucuronide (20 mg, **8**) [7], and quercetin-3,7-di-*O*-glucoside (15 mg, **9**) [8].

The BuOH fraction (3.5 g) was separated over polyamide, Sephadex LH-20, and RP-SiO_2 as above and by prep. HPLC [gradient mode (%B): 0–20 min, 5–23%; 20–45 min, 23–34%; 45–90 min, 34–52%] to isolate **1** (195 mg), **2** (173 mg), isorhamnetin-3-*O*-(2″-*O*-rhamnosyl-6″-*O*-glycosyl)-glucoside (14 mg, **10**) [5], kaempferol-3-*O*-neohesperidoside-7-*O*-glucoside (22 mg, **11**) [4], quercetin-3-*O*-(2″-*O*-rhamnosyl-6″-*O*-glucosyl)-glucoside (11 mg, **12**) [9], quercetin-3-*O*-neohesperidoside-7-*O*-glucoside (56 mg, **13**) [10], and quercetin-3-*O*-gentiobioside-7-*O*-glucuronide (12 mg, **14**) [7].

Quercetin-3-*O*-neohesperidoside-7-*O*-glucuronide (1). $C_{33}H_{38}O_{22}$. UV spectrum (70% MeOH, λ_{max}, nm): 255, 267 sh, 352; +NaOMe 270, 395; + NaOAc 264, 329 sh, 397; +$AlCl_3$ 272, 297 sh, 437; +$AlCl_3$/HCl 268, 295 sh, 360 sh, 403. HR-ESI-MS, *m*/*z* 787.4271 (calcd for $C_{33}H_{39}O_{22}$, 787.5990 $[M + H]^+$). ESI-MS, *m*/*z* (%): 787 $[M + H]^+$ (2), 641 $[(M + H) – C_6H_{10}O_4]^+$ (40), 479 $[(M + H) – C_6H_{10}O_4 – C_6H_{10}O_5]^+$ (100), 303 $[(M + H) – C_6H_{10}O_4 – C_6H_{10}O_5 – C_6H_8O_6]^+$ (4). Table 1 gives the PMR spectrum (500 MHz, MeOH-d_4, 298 K, δ, ppm) and ^{13}C NMR spectrum (125 MHz, MeOH-d_4, 298 K, δ, ppm).

Kaempferol-3-*O*-neohesperidoside-7-*O*-glucuronide (2). $C_{33}H_{38}O_{21}$. UV spectrum (70% MeOH, λ_{max}, nm): 265, 347; +NaOMe 242, 270, 345 sh, 385; + NaOAc 265, 379; +$AlCl_3$ 272, 301 sh, 352, 401; +$AlCl_3$/HCl 272, 300 sh, 348, 401. HR-ESI-MS, *m*/*z*: 771.5742 (calcd for $C_{33}H_{39}O_{21}$, 771.6000 $[M + H]^+$). ESI-MS, *m*/*z* (%): 771 $[M + H]^+$ (20), 625 $[(M + H) – C_6H_{10}O_4]^+$ (22), 463 $[(M + H) – C_6H_{10}O_4 – C_6H_{10}O_5]^+$ (100), 287 $[(M + H) – C_6H_{10}O_4 – C_6H_{10}O_5 – C_6H_8O_6]^+$ (5). Table 1 gives the PMR spectrum (500 MHz, MeOH-d_4, 298 K, δ, ppm) and ^{13}C NMR spectrum (125 MHz, MeOH-d_4, 298 K, δ, ppm).

Total hydrolysis was performed in TFA (2 M) followed by separation of the reaction mixture over polyamide [16] and analysis of the hydrolysis products by GC-MS (aglycons) [17], derivatization with 3-methyl-1-phenyl-2-pyrazolin-5-one and reductive amination with L-tryptophan [18] (monosaccharides of the D/L-series) [19]. The hydrolysis products of **1** included quercetin [20], D-glucose, L-rhamnose, and D-glucuronic acid; of **2**, kaempferol [20], D-glucose, L-rhamnose, and D-glucuronic acid.

Hydrolysis with β-glucosidase and α-rhamnosidase was conducted as described earlier [16]. Hydrolysis by β-glucosidase did not change **1** and **2**. The products from hydrolysis of **1** by α-rhamnosidase consisted of quercetin-3-*O*-glucoside-7-*O*-glucuronide (**8**) [7]; of **2**, kaempferol-3-*O*-glucoside-7-*O*-glucuronide (**5**) [7], which were identified using UV and NMR spectroscopic and mass spectrometric data.

Quercetin-3-*O*-glucoside-7-*O*-glucuronide (8). $C_{27}H_{28}O_{18}$. UV spectrum (70% MeOH, λ_{max}, nm): 256, 268 sh, 351; +NaOMe 271, 396; + NaOAc 263, 330 sh, 399; +$AlCl_3$ 271, 298 sh, 435; +$AlCl_3$/HCl 270, 296 sh, 361 sh, 401. HR-ESI-MS, *m*/*z*: 641.0231 (calcd for $C_{27}H_{29}O_{18}$, 641.4674 $[M + H]^+$). ESI-MS, *m*/*z* (%): 641 $[M + H]^+$ (12), 479 $[(M + H) – C_6H_{10}O_5]^+$ (100), 303 $[(M + H) – C_6H_{10}O_5 – C_6H_8O_6]^+$ (18). ^1H NMR spectrum (500 MHz, MeOH-d_4, 298 K, δ, ppm, J/Hz)*: 6.45 (1H, d, J = 2.1, H-6), 6.78 (1H, d, J = 2.1, H-8), 7.91 (1H, d, J = 2.1, H-2′), 6.89 (1H, d, J = 9.0, H-5′), 7.50 (1H, dd, J = 2.1, 9.0, H-6′), 12.53 (1H, br.s, 5-OH)**, 9.55 (1H, br.s, 3′-O<u>H</u>)**, 9.70 (1H, br.s, 4′-O<u>H</u>)**; 3-*O*-β-*D*-glucopyranose – 5.31 (1H, d, J = 7.2, H-1″), 3.70 (1H, m, H-2″), 3.55 (1H, m, H-3″), 3.48 (1H, m, H-4″), 3.61 (1H, m, H-5″), 3.90 (1H, dd, J = 2.1, 12.0, H_A-6″), 3.79 (1H, m, H_B-6″); 7-*O*-β-*D*-glucuronopyranose – 5.10 (1H, d, J = 7.5, H-1‴), 3.52 (1H, m, H-2‴), 3.38 (1H, m, H-3‴), 3.45 (1H, m, H-4‴), 4.08 (1H, d, J = 9.0, H-5‴). ^{13}C NMR spectrum (125 MHz, MeOH-d_4, 298 K, δ, ppm): 157.6 (C-2), 133.3 (C-3), 177.5 (C-4), 160.1 (C-5), 99.3 (C-6), 162.9 (C-7), 94.6 (C-8), 156.2 (C-9), 105.7 (C-10), 120.4 (C-1′), 115.2 (C-2′), 144.0 (C-3′), 148.7 (C-4′), 116.1 (C-5′), 121.4 (C-6′); 3-*O*-β-*D*-glucopyranose – 102.6 (C-1″), 74.2 (C-2″), 78.1 (C-3″), 70.4 (C-4″), 77.7 (C-5″), 60.5 (C-6″); 7-*O*-β-*D*-glucuronopyranose – 99.7 (C-1‴), 73.2 (C-2‴), 75.6 (C-3‴), 71.4 (C-4‴), 75.2 (C-5‴), 171.1 (C-6‴).

Kaempferol-3-*O*-glucoside-7-*O*-glucuronide (5). $C_{27}H_{28}O_{17}$. UV spectrum (70% MeOH, λ_{max}, nm): 266, 345; +NaOMe 241, 272, 341 sh, 381; + NaOAc 266, 375; +$AlCl_3$ 272, 300 sh, 351, 400; +$AlCl_3$/HCl 272, 301 sh, 347, 400. HR-ESI-MS, *m*/*z*: 625.0967 (calcd for $C_{27}H_{29}O_{17}$, 625.4684 $[M + H]^+$). ESI-MS, *m*/*z* (%): 625 $[M + H]^+$ (33), 463 $[(M + H) – C_6H_{10}O_5]^+$ (100), 287 $[(M + H) – C_6H_{10}O_5 – C_6H_8O_6]^+$ (12).

Oxidation by H_2O_2. A weighed portion (5 mg) of a compound was suspended in a mixture (10 mL) of H_2O_2 (40%)–NH_3 (25%)–H_2O (75:14:11), incubated at 25°C for 48 h, treated with catalase (100 U, 1.11.1.6, ≥10,000 U/mg, No. C40; Sigma-Aldrich), and passed after 2 h through Amberlyst® 15 (H^+-form, Sigma-Aldrich) that was eluted with H_2O (100 mL). The aqueous eluate was concentrated and analyzed by HPLC on a Milichrom A-02 chromatograph (EcoNova, Novosibirsk, Russia) equipped with a Separon SGX NH_2 column (2 × 75 mm, ∅ 5 μm; Tessek Ltd., Prague, Czech Rep.) in isocratic mode (MeCN–H_2O, 75:25, flow rate 100 μL/min) at column temperature 30°C with UV detection (λ 190 nm).

*Compound **8** was previously characterized only from hydrolysis results and UV spectroscopy [7], PMR and ^{13}C NMR spectroscopic data are given for the first time; **data obtained from DMSO-d_6 solutions.

The degradation products of **1** and **2** included neohesperidose (2-*O*-rhamnosylglucose, t_R 25.43 min), the retention time of which differed from that of isomeric rutinose (6-*O*-rhamnosylglucose, t_R 27.14 min).

Hydrolysis by β-Glucuronidase. A weighed portion of compound (10 mg) was dissolved in DMSO (50 μL), treated with phosphate buffer (990 μg, pH 5.0) and β-glucuronidase from *Helix pomatia* (100 U, HP-2, 3.2.1.31, ≥100,000 U/mL; No. G7017, Sigma-Aldrich), and incubated at 37°C for 3 h. Then, the mixture was treated with Me_2CO (4 mL) and centrifuged. The supernatant was concentrated to dryness under vacuum. The dry solid was separated over polyamide (50 g) with elution by H_2O (100 mL) and EtOH (70%, 200 mL). The EtOH eluate after hydrolysis of **1** held quercetin-3-*O*-neohesperidoside (calendoflavobioside, 5 mg) [11]; of **2**, kaempferol-3-*O*-neohesperidoside (6 mg, **6**) [4].

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