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FLAVONOID OLIGOSIDES FROM GEORGIAN *Astragalus falcatus*

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New flavonoid oligosides were isolated from leaves and flowers of Astragalus falcatus *Lam. It was found on the basis of chemical transformations, UV, IR, PMR, ^{13}C NMR, HMBC, HSQC, 1D-TOCSY, and mass spectral properties that falcoside C had the structure quercetin 3-O-[β-D-glucopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)]-β-D-galactopyranoside 7-O-β-D-glucopyranoside; falcoside D, isorhamnetin 3-O-[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)]-β-D-galactopyranoside 7-O-α-L-rhamnopyranoside.*

Keywords: *Astragalus falcatus*, flavonoids, flagalosides, quercetin, isorhamnetin, falcosides; UV, IR, PMR, ^{13}C NMR, 2M (HSQC, HMBC, 1D-TOCSY) spectra.

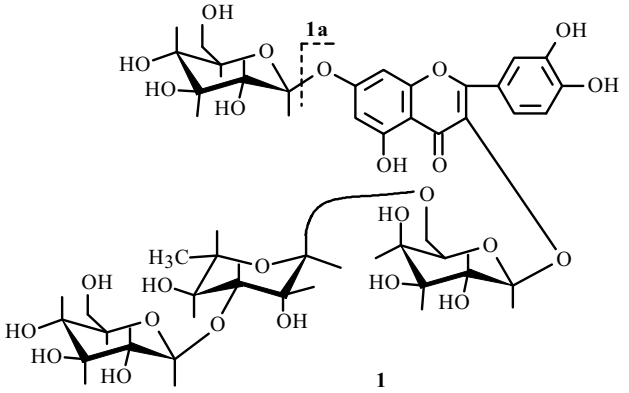
We reported previously on flavonoids from leaves and flowers of *Astragalus falcatus* Lam. (Leguminosae L.) inhabiting Georgia [1]. The plant is the official raw material for producing the substance for the drug flaronin with hypoazotemic and diuretic activity [2, 3]. The raw material contains robinin trioside (trade name flaronin) and highly polar compounds as impurities (up to 5%) in flaronin substance [2]. These glycosides are difficult to isolate because they are highly hydrophilic.

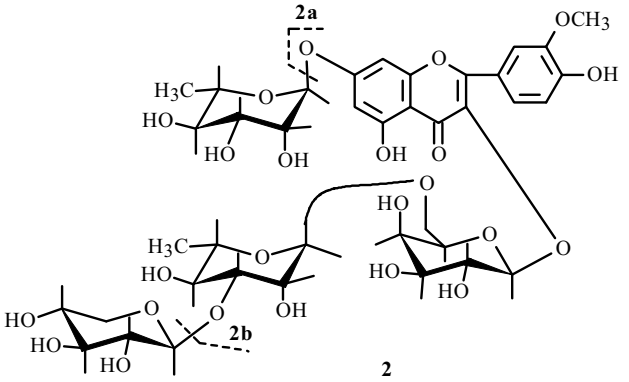
The components could be separated (see Experimental) from the total polar flavonoids that were isolated by preparative paper chromatography (PC) by using reversed-phase HPLC. The obtained compounds were denoted falcosides A-E. The individual components were analyzed in order to determine their structures after they were accumulated in significant amounts.

It was found that falcosides A, B, and E were oligosides of kaempferol with sugar components such as D-glucose, D-galactose, L-arabinose, and L-rhamnose in falcoside A; D-glucose, D-galactose, D-xylose, and L-rhamnose in falcoside B; and D-glucose, D-galactose, L-arabinose, D-xylose, and L-rhamnose in falcoside E.

The structures of falcosides C and D were elucidated on the basis of UV, IR, PMR, ^{13}C NMR, HMBC, HSQC, and 1D-TOCSY spectroscopy and mass spectrometry.

Falcoside C was a yellow powder that gave a positive Shinoda reaction [4] and negative Bryant test [5]. The molecular weight 934 (mass spectrometry) corresponded to the formula $C_{39}H_{50}O_{26}$. The IR spectrum showed absorption bands characteristic of flavonoids at 3600 cm^{-1} (OH) and 1650 (γ-pyrone C=O). The compound was designated as a flavonol glycoside based on absorption maxima in the UV spectrum in EtOH at 360 and 255 nm.





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The glycoside was hydrolyzed by H_2SO_4 solution (2%) to afford the aglycon (32%) with mp 316–319°C. Comparison with an authentic sample identified it as quercetin [6]. The carbohydrate part of the hydrolysate contained D-glucose, D-galactose, and L-rhamnose according to PC. A comparison of UV spectra of the glycoside and the aglycon that were taken with added diagnostic reagents showed that carbohydrate units were present on C-3 and C-7 of the aglycon (Experimental). Thus, flavonoid C was a bisdesmoside.

Treatment of compound C with aqueous base (0.5%) [7] gave D-glucose and an intermediate (**1a**) that formed after isolation, purification, and acid hydrolysis quercetin, D-galactose, D-glucose, and L-rhamnose. Therefore, glycoside C included two D-glucoses, one of which was bonded to C-7 of the aglycon; the other, in a triose on C-3 of the same genin.

Resonances belonging to four anomeric protons of carbohydrates were visible in the PMR spectrum taken in CD_3OD. This indicated unambiguously that the glycoside contained four sugar molecules. The chemical shifts of all carbohydrate protons were found using 1D-TOCSY and COSY experiments. Then, chemical shifts of the corresponding C atoms were found using HSQC (^1H–^{13}C) correlations.

Protons of sugars resonated in the PMR spectrum of falcoside C as doublets at 4.80 ppm with SSCC J = 7.6 Hz (D-glucose H-1), 5.21 with SSCC J = 8.3 Hz (D-galactose H-1), 5.60 with SSCC J = 7.6 Hz (D-glucose H-1), and 4.63 with SSCC J = 2.1 Hz (L-rhamnose H-1). This indicated that the monosaccharide units had the pyranose form. Monosaccharides of the D-series had the $^4C_1$-conformation and β-configuration; of the L-series, $^1C_4$-conformation and L-configuration [8-10].

The chemical shifts of C atoms of β-D-glucopyranose units indicated that they were located in terminal positions.

The HMBC spectrum of **1** (Table 1) showed a correlation peak between the resonance of the β-D-glucopyranoside anomeric proton and C-7 of the genin. This determined unambiguously the attachment site in the same position of quercetin. Alkaline hydrolysis of falcoside C, as expected, formed the progenin (**1a**) and D-glucose.

The sequence of carbohydrate attachment in the triose on C-3 of the aglycon was found using the HMBC correlation spectrum of falcoside C.

The HMBC spectrum showed a correlation peak between resonances of the D-galactose anomeric proton and C-3 of the genin. Thus, the D-galactose was bonded directly to the aglycon. The resonance of C-6 of the D-galactose unit in the ^{13}C NMR spectrum experienced a glycosylation effect and appeared at δ 66.80 ppm. This indicated that it was substituted with a carbohydrate [9–11].

Atom C-3 of L-rhamnose underwent a glycosylation effect in the ^{13}C NMR spectrum (δ 80.43). This indicated unambiguously that the L-rhamnose was the unifying unit in the triose. In fact, cross peaks between resonances of L-rhamnose H-1 with D-galactose C-6 and L-rhamnose C-3 with D-glucose H-1 were observed in the HMBC spectrum of falcoside C.

The chemical shifts of L-rhamnose C-3 and its adjacent C atoms (C-2, 75.78; C-4, 70.12 ppm) also indicated that this position was substituted [11]. This meant that the second D-glucose was bonded to L-rhamnose C-3.

Thus, glucoside C had the structure quercetin 3-*O*-[β-D-glucopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)]- β-D-galactopyranoside 7-*O*-β-D-glucopyranoside.

Falcoside D was also a flavonol glycoside according to its UV spectrum with absorption maxima at 375 and 275 nm. The IR spectrum had absorption bands at 3500–3600 cm^{-1} (OH) and 1655 (γ-pyrone C=O) and also confirmed that this glycoside was a flavonoid.

The glycoside was hydrolyzed by acid (2% H_2SO_4) to form the aglycon (~30%) that was identified as isorhamnetin according to the alkali fusion products (phloroglucinol and vanillic acid), mp 300–302°C, and comparison with an authentic sample [3]. D-Galactose, L-rhamnose, and D-xylose were detected in the carbohydrate part of the glycoside. Judging from the yield of genin from the acid hydrolysate, glycoside **2** contained four carbohydrate molecules. In fact, the PMR spectrum exhibited resonances for four anomeric protons.

Glycoside D was cleaved by alkaline solution (0.5%) into L-rhamnose and an intermediate (**2a**) that formed isorhamnetin, D-galactose, L-rhamnose, and D-xylose after isolation, purification, and acid hydrolysis. Thus, the glycoside structure included two L-rhamnoses, one of which was bonded to isorhamnetin C-7; the other, to a triose on C-3 of the same genin. Thus, this glycoside was also a bisdesmoside.

The bonding sequence of the carbohydrates in the triose was found by analyzing PMR, ^{13}C NMR, and HMBC spectra and products of chemical transformation of glycoside D. The HMBC spectrum (^1H–^{13}C) contained a correlation peak between resonances of the D-galactose anomeric proton and C-3 of the genin. The correlation between resonances of the D-galactose and L-rhamnose units was analogous to that of the preceding compound, falcoside C. Thus, the D-galactose in the glycoside was bonded directly to the aglycon. The L-rhamnose was glycosylated also on C-3 because the chemical shift of C-3 was δ 80.39 ppm. The anomeric proton of D-xylose correlated with L-rhamnose C-3.

TABLE 1. PMR and ^{13}C NMR Data for Falcosides C (**1**) and D (**2**) (CD_3OD, δ, ppm, J/Hz)

C atom	**1**			**2**		
	δ_C	δ_H	HMBC	δ_C	δ_H	HMBC
2	157.05			157.75		
3	133.25			133.02		
4	177.34			177.14		
5	161.17			160.97		
6	97.54	6.3 (d, J = 2.2)	5, 7, 8, 10	96.94	6.0 (d, J = 2.2)	5, 7, 8, 10
7	162.80			161.60		
8	92.84	6.5 (d, J = 2.08)	6, 7, 9, 10	92.84	6.42 (d, J = 2.02)	7, 9, 10
9	157.27			156.07		
10	105.67			105.77		
1′	121.07			121.05		
2′	115.20	7.8 (d, J = 2.1)	2, 1′, 3′, 4′, 6′	113.90	7.93 (d, J = 2.20)	1′, 6′, 3′, 4′
3′	144.70			149.60		
4′	148.60			149.50		
5′	116.40	6.8 (d, J = 8.3)	1′, 3′, 4′, 6′	115.10	6.90 (d, J = 8.40)	6′, 4′, 1′
6′	121.60	7.8 (dd, J = 2.1; 8.2)	1′, 2, 2′, 5′	122.30	7.64 (dd, J = 2.2; 8.4)	2, 1′, 2′, 5′
OCH_3				55.60	3.81 s	3′
			7-*O*-*β*-D-Glc*p* unit			
1[a]	100.60	5.60 (d, J = 7.6)	7, 2[a]			
2[a]	73.00	3.85 (dd, J = 9.4; 8.0)	1[a], 3[a]			
3[a]	74.69	3.59 (dd, J = 9.4; 3.8)	1[a], 4[a], 5[a]			
4[a]	66.07	3.82 (dd, J = 10.0; 9.0)	3[a], 5[a]			
5[a]	77.80	3.70 m	1[a], 4[a], 6[a]			
6[a]	59.59	3.54 (dd, J = 12,1; 5.2)	5[a], 4[a]			
		3.70 (dd, J = 12.1; 2.2)				
			β-*D*-Gal*p* unit			
1[b]	103.49	5.21 (d, J = 8.3)	3, 2[b],3[b]	99.49	5.15 m	3, 2[b], 3[b]
2[b]	73.59	3.87 (dd, J = 9.4; 8.3)	1[b], 3[b]	73.42	3.86 (dd, J = 9.4; 8.3)	1[b], 3[b]
3[b]	74.72	3.55 (dd, J = 9.4; 3.8)	2[b], 4[b]	74.71	3.60 (dd, J = 9.4; 3.8)	2[b], 4[b]
4[b]	66.86	3.82 (dd, J = 2.9; 1.2)	3[b], 5[b]	66.85	3.83 (dd, J = 2.9; 1.2)	3[b], 5[b], 6[b]
5[b]	75.81	3.70 (m, J = 3.7)	4[b], 6[b]	75.82	3.71 m	4[b], 6[b]
6[b]	66.80	3.55; 3.74 m	1[c], 5[b]	66.79	3.75; 3.54 m	1[c], 5[b]
			α-L-Rha*p* unit on C-6 D-Gal*p*			
1[c]	96.39	4.63 (d, J = 2.1)	6[b], 2[c]	96.41	4.54 (d, J = 2.1)	6[b], 2[c]
2[c]	75.78	3.54 (dd, J = 3.4; 1.8)	1[c], 3[c]	75.76	3.78 (dd, J = 3.8; 2.1)	1[c], 3[c]
3[c]	80.43	3.49 (d, J = 9.0)	1[d], 2[c], 4[c]	80.39	3.57 (dd, J = 9.6; 3.8)	1[e], 2[c], 4[c]
4[c]	70.12	3.26 (t, J = 9.4)	3[c], 5[c], 6[c]	69.95	3.47 (t, J = 9.4)	3[c], 5[c], 6[c]
5[c]	68.04	3.50 (dd, J = 9.5; 6.0)	4[c], 6[c]	67.98	3.52 (dd, J = 9.5; 6.15)	4[c], 6[c]
6[c]	15.34	1.26 (d, J = 6.15)	5[c], 4[c]	15.37	1.92 (d, J = 6.2)	5[c], 4[c]
			β-D-Glc*p* unit on C-3 L-Rha*p*			
1[d]	104.50	4.80 (d, J = 7.6)	3[c], 2[d]			
2[d]	75.02	3.82 (dd, J = 9.4; 7.6)	1[d], 3[d]			
3[d]	76.85	3.56 (dd, J = 9.4; 3.8)	1[d], 4[d], 2[d],			
4[d]	69.71	3.80 (dd, J = 10.0; 9.0)	3[d], 5[d], 6[d]			
5[d]	78.66	3.70 m	1[d], 4[d], 6[d]			
6[d]	61.30	3.56 (dd, J = 12.0; 2.1)	1[d],5[d]			
		3.75 (dd, J = 12.0; 4.5)				
			β-D-Xyl*p* unit			
1[e]				105.68	4.68 (d, J = 7.0)	3[c], 2[e]
2[e]				75.50	3.20 (dd, J = 9.0; 7.3)	3[e], 4[e]
3[e]				77.63	3.32 (t, J = 9.0)	2[e], 4[e]
4[e]				72.56	3.45 m	3[e], 5[e]
5[e]				65.57	3.14 (dd, J = 9.0; 9.0)	3[e], 4[e]
					3.85 (dd, J = 10.5; 5.0)	
			7-*O*-*α*-L-Rha*p* unit			
1[f]				99.40	5.60 (d, J = 2.0)	7, 2[f]
2[f]				71.40	4.02 (dd, J = 3.5; 1.8)	1[f], 3[f]
3[f]				69.92	3.83 (dd, J = 9.4; 3.4)	2[f], 4[f],
4[f]				68.65	3.45 (t, J = 9.4)	3[f], 5[f]
5[f]				67.37	3.61 (dd, J = 9.4; 6.1)	4[f], 6[f]
6[f]				15.85	1.26 (d, J = 6.2)	5[f]

Spectral data confirmed that D-xylose and keioside (**2b**) [12] were formed by stepwise acid hydrolysis of intermediate **2a**. Thus, the bonding sequence of the carbohydrate units on C-3 of the aglycon was D-galactose-(6←1)-α-L-rhamnose-(3←1)-D-xylose. The SSCCs of the anomeric protons were consistent with the pyranose form of the monosaccharides; the $^4C_1$-conformation and β-configuration of monosaccharides of the D-series; and the $^1C_4$-conformation and α-configuration of L-series monosaccharides. Therefore, falcoside D was characterized as isorhamnetin 3-*O*-[β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→6)]- β-D-galactopyranoside 7-*O*-α-L-rhamnopyranoside.

Falcosides C and D were new compounds.

D-Galactose and L-rhamnose are often encountered as robinobioses in flavonoid glycosides isolated by us [1, 3, 11]. Apparently this is a characteristic signature of flavonoids from *Astragalus* growing in Georgia.

EXPERIMENTAL

General Comments. Mother liquors remaining after crystallization of robinin (flaronin) that were obtained from the aqueous alcohol extract of leaves and flowers of *A. falcatus* were used for the analysis. HPLC (Agilent HP 1000, Palo Alto, CA) with an XTerra column (7.8 × 300 mm) packed with Silicagel RP-18 sorbent (particle size 5 μm) and mobile phase flow rate 2 mL/min were used to separate and accumulate the compounds. PC was carried out on FN 11 paper using solvent systems BuOH:HOAc:H_2O (4:1:2, 1), Py:benzene:BuOH:H_2O (3:1:5:3, 2), and HOAC (15%, 3). Monosaccharides were detected in chromatograms by anilinium phthalate.

IR spectra were recorded in KBr on a UR-20 instrument; UV spectra, on an SF-16 spectrophotometer (Lomo); NMR spectra, in CD_3OD on Bruker AM-400 and DRX-500 instruments.

Mass spectra were recorded in a Thermo Finnigan instrument (San Jose, CA, USA). A solution of the compound in CD_3OD was injected at 3 μL/min. The potential on the capillary was 40 V; of the solvent stream, 4.8 kV. The capillary temperature was 220°C. Data were calculated based on positive ions.

Isolation of Flavonoids. Robinin mother liquor (2.2 L) was condensed to 100 mL. Portions (0.1 mL each) were placed on chromatographic paper for preparative separation. Chromatography was performed using solvent system 1. Glycosides were eluted from the chromatograms by EtOH (30%). The EtOH extracts were evaporated to produce total highly polar flavonoids (202 mg) with a very low content of robinin. Portions (5 mg each) of these flavonoids were dissolved in MeOH:H_2O (1:3, 100 μL) and injected into the chromatograph. The mobile phase consisted of binary CH_3CN:H_2O mixtures (from 10:90 to 30:70). The run time was 60 min. The retention time of falcoside A was 11.0 min; falcoside B, 11.4; robinin, 11.83; falcoside C, 31.9; falcoside D, 33.7; and falcoside E, 36.2.

All together we isolated 8 mg of falcoside A; 11, falcoside B; 42, falcoside C; 38, falcoside D; 5, falcoside E; and 55, robinin.

Acid Hydrolysis of Falcosides A, B, and E. Compounds (8, 11, and 5 mg, respectively) were hydrolyzed separately by aqueous H_2SO_4 (2%). Algycons were extracted from the resulting reaction mixture by EtOAc. The combined EtOAc extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated. The solid was dissolved in EtOH and chromatographed using PC and system 1. Aglycons of falcosides A, B, and E turned out to be identical with mp 275–278°C and appeared on PC at the level of authentic kaempferol [3].

The aqueous part of the hydrolysates of falcosides A, B, and E gave qualitative evidence for D-glucose, D-galactose, L-arabinose, and L-rhamnnose for falcoside A; D-glucose, D-galactose, and D-xylose for falcoside B; and D-glucose, D-galactose, L-arabinose, and L-rhamnose for falcoside E.

Falcoside C, yellow powder, MW 934, $C_{39}H_{50}O_{26}$; soluble in aqueous alcohol (35–40%). UV spectrum (EtOH, λ_{max}, nm): 360, 255; +CH_3COONa: 372, 260; +$AlCl_3$: 420, 275; +$AlCl_3$/HCl: 402, 363sh, 272. IR spectrum (KBr, cm^{-1}): 3600 (OH), 1660–1650 (γ-pyrone C=O), 1550 (>C=C<). Mass spectrum (EI, 40 eV, *m*/*z*, I_{rel}, %): 935 (3.9) $[M + H]^+$, 773 (7.9) $[M + H - 162]^+$, 611 (21) $[M + H - 162 \times 2]^+$, 465 (14.5) $[M + H - 162 \times 2 - 146]^+$, 429 (100) $[M + H - 162 \times 2 - 146 - 2 \times H_2O]^+$, 303 (31.6) $[M + H - 162 \times 2 - 146 - 162]^+$.

Table 1 presents PMR and ^{13}C NMR data.

Acid Hydrolysis of Falcoside C. The compound (20 mg) was hydrolyzed by H_2SO_4 solution (2%, 10 mL). The hydrolysis was monitored by PC using system 3. The aglycon was extracted from the reaction mixture using EtOAc. The EtOAc extract was dried and evaporated. The solid (5.8 mg, 32%) was dissolved in alcohol and crystallized to afford the

aglycon, mp 302–305°C. A mixed sample with quercetin did not show melting point depression. IR spectrum (KBr, cm^{-1}): 3600 (OH), 1665 (γ-pyrone C=O), 1556 (>C=C<). UV spectrum (EtOH, λ_{max}, nm): 370, 269, 255; +CH_3COONa: 380, 273; +$AlCl_3$: 455, 276; +$AlCl_3$/HCl: 430, 273.

The aqueous part of the hydrolysate was neutralized with AV-17 anion-exchanger (OH^--form), evaporated, and chromatographed using system 2. D-Glucose, D-galactose, and L-rhamnose were detected.

Alkaline Hydrolysis of Falcoside C. The compound (15 mg) was dissolved in NaOH solution (12 mL, 0.5%) and hydrolyzed as before [7]. When the hydrolysis was finished the reaction mixture was neutralized to pH 7 and extracted with EtOAc:EtOH (4:1). The extracts were dried to afford a solid (10 mg). D-Glucose was detected by PC in the aqueous part of the hydrolysate.

The solid intermediate **1a** was hydrolyzed by acid analogously as above to afford the genin quercetin. The carbohydrate part contained D-glucose, D-galactose, and L-rhamnose.

Falcoside D, yellow powder, MW 902, $C_{39}H_{50}O_{24}$, soluble in aqueous alcohol (35-40%). UV spectrum (EtOH, λ_{max}, nm): 375, 275; +CH_3COONa: 360, 285sh, 260; +$AlCl_3$: 400, 268, 300sh; +$AlCl_3$/HCl: 398, 267, 300sh. IR spectrum (KBr, cm^{-1}): 3600 (OH), 1660–1655 (γ-pyrone C=O), 1552 (>C=C<). Mass spectrum (EI, 40 eV, m/z, I_{rel}, %): 903 (23.6) $[M + H]^+$, 757 (21) $[M + H - 146]^+$, 625 (21) $[M + H - 146 - 132]^+$, 479 (52.6) $[M + H - 146 - 132 - 146]^+$, 395 (100) $[M + H - 132 - 162 - 146 - 2 \times H_2O - OCH_3]^+$, 317 (18.4) $[M + H - 146 \times 2 - 132 - 162]^+$.

Table 1 presents the PMR and ^{13}C NMR spectra.

Acid Hydrolysis of Falcoside D. The compound (12 mg) was hydrolyzed by H_2SO_4 solution (2%, 13 mL). The hydrolysis was monitored by PC using systems 1 and 3. The hydrolysis was complete after 48 min. The aglycon was extracted from the reaction mixture by EtOAc. The extract was dried and evaporated. The solid (3.6 mg, 29%) was crystallized from alcohol to afford the aglycon, mp 299–302°C. A mixed sample with isorhamnetin did not give melting point depression.

D-Galactose, D-xylose, and L-rhamnose were detected in the aqueous part of the hydrolysate after the appropriate work up (see above).

Alkaline Hydrolysis of Falcoside D. The compound (15 mg) was hydrolyzed analogously to falcoside C [7]. The extracts were condensed to afford intermediate **2a** (9 mg). L-Rhamnose was detected in the aqueous part of the hydrolysate by PC.

Acid Hydrolysis of Intermediate 2a. The glycoside (5 mg) was hydrolyzed by acid analogously as described above to afford the genin isorhamnetin (2.1 mg). D-Galactose, D-xylose, and L-rhamnose were detected in the carbohydrate part by PC using system 2.

Stepwise Acid Hydrolysis of Intermediate 2a. Intermediate **2a** (4 mg) was hydrolyzed by the literature method [13]. D-Xylose and glycoside **2b**, mp 184–187°C, were detected in the aqueous part of the hydrolysate by PC using system 2. The glycoside appeared at the level of authentic keioside by PC using system 1 [12].

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