

## FLAVONOID GLYCOSIDES FROM THE AERIAL PART OF *Lespedeza tomentosa*

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The aerial part of *Lespedeza tomentosa* (Thunb.) Maxim. growing in southern Primorsky Krai, Russian Federation, yielded 10 identified flavonoid glycosides, eight of which were observed for the first time in this plant. The structures of the two new compounds were elucidated based on NMR spectroscopy and mass spectrometry as morin 3-O-rutinoside and 3-O-(2-O- $\alpha$ -L-rhamnopyranosyl)- $\beta$ -D-galactopyranoside.

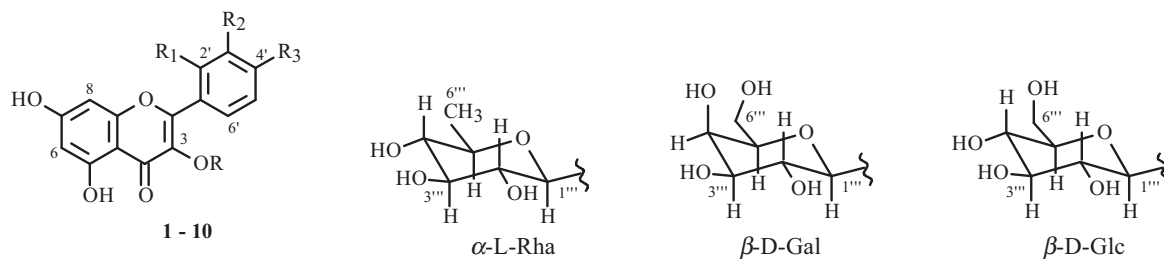
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Plants of the genus *Lespedeza* (Fabaceae, Leguminosae) are wild bushes including ~50 species. The genus *Lespedeza* in Russia is represented by five species growing in southern East Siberia, the Far East, Primorye, and Priamurye. Most useful biologically active flavonoids in these plants are found in the aerial part of the bush (in runners, flowers, leaves) [1]. However, several species of this genus, e.g., *L. bicolor*, contain flavonoids in stem and root bark [2, 3].

Previously the aerial part of *L. tomentosa* collected in China yielded 13 identified flavonoids including isorhamnetin 3-O-rutinoside and 3-O-neohesperidoside; quercetin 3-O-glucoside; kaempferol 3-O-robinobioside and 3-O-rhamnosyl-(1 $\rightarrow$ 2)-galactoside [1], trifolin (kaempferol 3-O- $\beta$ -D-galactopyranoside) [4], apigenin, luteolin, orientin (luteolin 8-C-glucoside), homoorientin (luteolin 6-C-glucoside), saponaretin (isovitexin, apigenin 6-C-glucoside), vitexin (apigenin 8-C-glucoside), and luteolin 7-glucoside [5].

The goal of the present work was to isolate and elucidate the structures of flavonoids from *L. tomentosa* (Thunb.) Maxim. growing in south Primorsky Krai, Russian Federation.

Chromatography of the EtOH extract of *L. tomentosa* over various sorbents afforded 10 pure flavonoid glycosides (1–10).



- 1:** R =  $\alpha$ -L-Rha(1 $\rightarrow$ 6)- $\beta$ -D-Glc, R<sub>1</sub> = R<sub>2</sub> = H, R<sub>3</sub> = OH; **2:** R =  $\alpha$ -L-Rha(1 $\rightarrow$ 2)- $\beta$ -D-Glc, R<sub>1</sub> = R<sub>2</sub> = H, R<sub>3</sub> = OH  
**3:** R =  $\alpha$ -L-Rha(1 $\rightarrow$ 6)- $\beta$ -D-Glc, R<sub>1</sub> = H, R<sub>2</sub> = OCH<sub>3</sub>, R<sub>3</sub> = OH; **4:** R =  $\beta$ -D-Glc, R<sub>1</sub> = H, R<sub>2</sub> = R<sub>3</sub> = OH  
**5:** R =  $\beta$ -D-Glc, R<sub>1</sub> = R<sub>3</sub> = OH, R<sub>2</sub> = H; **6:** R =  $\alpha$ -L-Rha(1 $\rightarrow$ 6)- $\beta$ -D-Glc, R<sub>1</sub> = H, R<sub>2</sub> = R<sub>3</sub> = OH  
**7:** R =  $\alpha$ -L-Rha(1 $\rightarrow$ 6)- $\beta$ -D-Glc, R<sub>1</sub> = R<sub>3</sub> = OH, R<sub>2</sub> = H; **8:** R =  $\alpha$ -L-Rha(1 $\rightarrow$ 2)- $\beta$ -D-Gal, R<sub>1</sub> = H, R<sub>2</sub> = R<sub>3</sub> = OH  
**9:** R =  $\alpha$ -L-Rha(1 $\rightarrow$ 2)- $\beta$ -D-Gal, R<sub>1</sub> = R<sub>3</sub> = OH, R<sub>2</sub> = H; **10:** R = 2'',6''-di- $\alpha$ -L-Rha- $\beta$ -D-Gal, R<sub>1</sub> = H, R<sub>2</sub> = R<sub>3</sub> = OH

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TABLE 1. LC-MS Parameters (HPLC-UV–HR-MS) of Flavonoids 1–10

Compound (formula)	RT, min	$\lambda_{\max}$	Molecular ions, $m/z$			
			$[M - H]^-$		$[M + H]^+$	
			calculated	measured	calculated	measured
<b>1</b> (C <sub>27</sub> H <sub>30</sub> O <sub>15</sub> )	25.87	265, 347	593.1506	593.1491	595.1663	595.1650
<b>2</b> (C <sub>27</sub> H <sub>30</sub> O <sub>15</sub> )	26.85	265, 347	593.1506	593.1473	595.1663	595.1665
<b>3</b> (C <sub>28</sub> H <sub>32</sub> O <sub>16</sub> )	27.58	253, 354	623.1612	623.1587	625.1769	625.1760
<b>4</b> (C <sub>21</sub> H <sub>20</sub> O <sub>12</sub> )	25.21	255, 353	463.0876	463.0856	465.1033	465.1059
<b>5</b> (C <sub>21</sub> H <sub>20</sub> O <sub>12</sub> )	24.74	256, 350	463.0876	463.0842	465.1033	465.1075
<b>6</b> (C <sub>27</sub> H <sub>30</sub> O <sub>16</sub> )	24.06	265, 354	609.1456	609.1447	611.16121	611.1572
<b>7</b> (C <sub>27</sub> H <sub>30</sub> O <sub>16</sub> )	24.06	255, 354	609.1456	609.1447	611.16121	611.1572
<b>8</b> (C <sub>27</sub> H <sub>30</sub> O <sub>16</sub> )	22.86	255, 354	609.1456	609.1425	611.1612	611.1640
<b>9</b> (C <sub>27</sub> H <sub>30</sub> O <sub>16</sub> )	23.20	255, 353	609.1456	609.1440	611.1612	611.1657
<b>10</b> (C <sub>33</sub> H <sub>40</sub> O <sub>20</sub> )	21.65	256, 350	755.2035	755.2028	757.2191	757.2176

Compounds **1** and **2** according to HPLC-UV–HR-MS had the same formula C<sub>27</sub>H<sub>30</sub>O<sub>15</sub> but different retention times (RTs) (Table 1). An analysis of <sup>1</sup>H and <sup>13</sup>C NMR, HSQC, HMBC, and COSY spectra identified **1** and **2** as kaempferol 3-*O*-rutinoside (nicotiflorin) [6] and kaempferol 3-*O*-neohesperidoside [7], respectively. Flavonoid **3** had the longest RT (27.58) and formula C<sub>28</sub>H<sub>32</sub>O<sub>16</sub> and was identified by HPLC-UV–HR-MS (Table 1) as isorhamnetin 3-*O*-rutinoside, which was isolated earlier from this plant by Japanese researchers [1].

Flavonoids **4** and **5** had identical formulas (C<sub>21</sub>H<sub>20</sub>O<sub>12</sub>) but different HPLC RTs (Table 1). They were quercetin 3-*O*- $\beta$ -D-glucoside (**4**) [8] and morin 3-*O*- $\beta$ -D-glucoside (**5**) [9] according to <sup>1</sup>H and <sup>13</sup>C NMR spectra and the literature.

Quercetin 3-*O*- $\beta$ -D-glucopyranoside (isoquercitrin, hirsutrin) (**4**) was already isolated earlier from the aerial part of *L. tomentosa* [1]. Compound **4** is known to possess hepatoprotective properties and to occur in other *Lespedeza* spp. [10]. Morin 3-*O*- $\beta$ -D-glucopyranoside (**5**), which was isolated earlier from *Acridocarpus orientalis* and *Solena amplexicaulis* [9], was observed in *L. tomentosa* for the first time by us. Compound **5** is known to exhibit significant cytotoxicity for HL60 tumor cells [11] and to inhibit growth of pathogenic fungi [9].

Compounds **6** and **7** gave UV spectra with two absorption maxima and formulas C<sub>27</sub>H<sub>30</sub>O<sub>16</sub>, corresponding to flavonoid diglycosides (Table 1). NMR spectral data for the carbohydrate fragments of **6** and **7** were the same. Compound **7** according to <sup>1</sup>H and <sup>13</sup>C NMR spectra contained a disaccharide bonded to the C-3 hydroxyl with two anomeric protons at  $\delta$  5.31 ppm (d,  $J = 7.5$  Hz) and 4.42 ppm (d,  $J = 1.1$  Hz) that were characteristic of glucose and rhamnose, respectively (Table 2).

However, ring B in **7**, in contrast to rutin (**6**), had hydroxyls bonded to C-2' and C-4' C atoms, which was confirmed by an ABX spin system in its PMR spectrum that consisted of three resonances of aromatic protons at  $\delta$  7.53 ppm (d,  $J = 2.0$  Hz), 7.64 ppm (dd,  $J = 2.1, 8.4$  Hz), and 6.82 ppm (d,  $J = 8.5$  Hz) (Table 2). Therefore, the structure of **7** was morin 3-*O*-rutinoside.

Rutin (**6**) is known to possess antidiabetic; anticoagulant; antiviral; cardio-, nephro-, and hepatoprotective; and other useful pharmacological properties [12].

Flavonoids **8** and **9** had the same formulas (C<sub>21</sub>H<sub>20</sub>O<sub>12</sub>) according to HPLC-UV–HR-MS spectra (Table 1) and different RTs. Flavonoid **8** was identified as quercetin 3-*O*-(2-*O*- $\alpha$ -L-rhamnopyranosyl)- $\beta$ -D-galactopyranoside [13]. The PMR spectrum of **9** contained resonances at  $\delta$  5.65 ppm (d,  $J = 7.8$  Hz) and 5.08 ppm (broad singlet) that were attributed to  $\alpha$ -rhamnopyranosyl and  $\beta$ -galactopyranosyl. The chemical shifts of the disaccharide resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra of **8** and **9** agreed fully (Table 2). This proved that the terminal sugar in **9** was  $\alpha$ -rhamnopyranose bonded to the 2-position of  $\beta$ -galactopyranose (Table 2). <sup>1</sup>H and <sup>13</sup>C NMR spectra of **8** and **9** differed in the positions of hydroxyls on ring B of their aglycons (Table 2).

The ring B OH groups in **9** were located on C-2' and C-4', which was confirmed by an ABX spin system in its PMR spectrum consisting of three resonances of aromatic protons at  $\delta$  7.52 ppm (d,  $J = 2.3$  Hz), 7.60 ppm (dd,  $J = 2.3, 8.5$  Hz), and 6.82 ppm (d,  $J = 8.9$  Hz) (Table 2). Therefore, the structure of **9** was established as morin 3-*O*-(2-*O*- $\alpha$ -L-rhamnopyranosyl)- $\beta$ -D-galactopyranoside.

TABLE 2. <sup>1</sup>H (700 MHz) and <sup>13</sup>C (176 MHz) NMR Spectra of **7** and **9** (DMSO-d<sub>6</sub>, δ, ppm, J/Hz)

C atom	<b>7</b>		<b>9</b>	
	δ <sub>H</sub>	δ <sub>C</sub>	δ <sub>H</sub>	δ <sub>C</sub>
2	–	156.5	–	156.3
3	–	133.5	–	133.4
4	–	177.5	–	177.5
5	–	161.4	–	161.3
6	6.19 (br.s)	98.7	6.19 (d, J = 2.1)	98.7
7	–	164.2*	–	164.2
8	6.38 (br.s)	93.46	6.38 (d, J = 2.1)	93.5
9	–	156.6*	–	156.4
10	–	103.9	–	104.0
OH	12.58		12.59	
1'	–	121.7	–	121.2
2'	–	144.9	–	144.8
3'	7.53 (d, J = 2.0)	116.3	7.52 (d, J = 2.3)	116.1
4'	–	148.6	–	148.0
5'	7.64 (dd, J = 2.1, 8.4)	122.0	7.60 (dd, J = 2.3, 8.5)	121.7
6'	6.82 (d, J = 8.5)	115.2	6.82 (d, J = 8.9)	115.2
1''	5.31 (d, J = 7.5)	102.1	5.65 (d, J = 7.8)	98.49
2''	3.26 (m)	73.1	3.79 (m)	75.0
3''	3.25 (m)	76.5	3.57 (m)	74.1
4''	3.05 (m)	70.5	3.63 (m)	68.6
5''	3.27 (m)	76.0	3.80 (m)	75.0
6''	3.63 (dd, J = 5.5, 11.4) 3.99 (dd, J = 3.9, 11.4)	67.0	3.42 (m) 3.27 (m)	63.15
1'''	4.42 (d, J = 1.1)	100.8	5.08 (br.s)	100.32
2'''	3.03 (m)	70.7	3.47 (m)	70.64
3'''	3.76 (m)	70.0	3.73 (m)	70.73
4'''	3.08 (m)	71.9	3.12 (m)	71.94
5'''	3.18 (m)	68.3	3.75 (m)	68.18
6'''	0.99 (3H, d, J = 6.2)	17.8	0.78 (3H, d, J = 6.1)	18.58

Flavonoid **10** had formula C<sub>33</sub>H<sub>40</sub>O<sub>20</sub> and the shortest RT (21.65) as compared to the other compounds (Table 1). An analysis of <sup>1</sup>H and <sup>13</sup>C NMR, HSQC, HMBC, and COSY spectra showed that **10** was a quercetin triglycoside. This was confirmed by three anomeric protons in its spectra at δ 5.57 (d, J = 7.8), 4.38 (br.s), and 5.09 (br.s). Glycoside **10** contained two α-L-rhamnopyranose residues bonded to the 2''- and 6''-positions of β-D-galactopyranose. Quercetin 3-O-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)-β-D-galactopyranoside] was first isolated from the aerial part of *Taverniera aegyptiaca* [14].

Thus, the chemical composition of flavonoids from *L. tomentosa* growing in southern Primorsky Krai, Russian Federation, differed considerably from plants of this species from other regions. The aerial part of *L. tomentosa* yielded 10 flavonol glycosides containing two mono-, seven di-, and one trisaccharide on C-3. Of these, two disaccharides were new. Their structures were established as morin 3-O-rutinoside (**7**) and morin 3-O-(2-O-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**9**).

## EXPERIMENTAL

UV spectra were recorded on a UV 1800 spectrophotometer (Shimadzu). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in DMSO-d<sub>6</sub> at 30°C using Bruker Avance III DRX-700 and Avance DRX-500 instruments (Bruker, Karlsruhe, Germany). HMBC spectra were optimized for 5 Hz. Analytical HPLC of fractions and pure compounds used an Agilent Technologies 1100 series chromatograph equipped with a Supelco C-18 column (75 × 3 mm, 3 μm) at 30°C. The solvent flow rate was 0.8 mL/min. Solution A (1% AcOH) and solution B (1% AcOH in MeCN) were used for gradient elution of samples with 10% B (2 min), 20% B (5 min), 30% B (15 min), 40% B (17 min), 50% B (20 min), 90% B (22 min), and 10% B (25 min).

Analytical HPLC-UV-HR-MS (high-resolution mass spectrometry) used a Shimadzu LCMS-IT-TOF LC-MS (Japan) equipped with an LC-20A HPLC, SPD-M20A diode-array detector, and time-of-flight mass spectrometer with an ion trap. Constituents of mixtures were separated over a Discovery HS C-18 column (150 × 2.1 mm, 3 mm) thermostatted at 36°C. UV spectra were recorded in the range  $\lambda$  200–800 nm. The mobile phase consisted of solutions of formic acid (0.1%) in deionized H<sub>2</sub>O (A) and MeCN (B). Gradient elution used flow rate 0.2 mL/min with 5% B (5 min), 5–40% B (45 min), 40–95% B (65 min), and 95% B (80 min). Mass spectrometric data were obtained with electrospray ionization and time-of-flight recording of negative and positive ions with resolution 12,000. The range of recorded *m/z* values was 200–1000. The drying gas (N<sub>2</sub>) pressure was 150 kPa. The spray-gas flow rate was 1.5 L/min. The ion source potential was –3.8 kV for recording positive ions and 4.5 kV for recording negative ions.

Aerial parts of *L. tomentosa* were collected in Primorsky Krai (Oktyabr'sky District, in the vicinity of Sinel'nikovo-1) in September 2020. The *L. tomentosa* plants were 80–100 cm high. Inflorescences of *L. tomentosa* had a milky tint with lilac bands. The flowers were usually milky- or cream-colored. The stems were covered with reddish-colored fibers. Herbarium specimen (voucher) No. 103616 is preserved in the Herbarium of PIBOC, FEB, RAS.

The dry EtOH extract (15 g) from dried stems and leaves of *L. tomentosa* was chromatographed over a column packed with polyamide 6 DF (Sigma-Aldrich) using CHCl<sub>3</sub> with a gradient of increasing EtOH content up to 100%. Obtained fractions of flavonoids were analyzed by HPLC, HPLC-UV-HR-MS, and subsequently chromatographed over a column packed with Toyopearl HW-10C using H<sub>2</sub>O–EtOH (40:60). Flavonoid fractions were additionally purified over YMC-GEL ODS-A sorbent using H<sub>2</sub>O with a gradient of increasing EtOH content from 20 to 100% to give the 10 flavonoid glycosides **1–10** in yields of 2.8, 2.6, 3.0, 4.1, 3.2, 8.0, 2.3, 3.4, 2.5, and 6.0 mg.

**Kaempferol 3-O-rutinoside (1)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data. <sup>1</sup>H NMR (700 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm, J/Hz): 12.48 (1H, br.s, 5-OH), 7.97 (2H, d, J = 8.7, H-2', 6'), 6.86 (2H, d, J = 8.7, H-3', 5'), 6.29 (1H, br.s, H-8), 6.09 (1H, br.s, H-6), 5.26 (1H, d, J = 7.6, H-1''), 4.39 (1H, d, J = 1.1, H-1'''), 3.69 (2H, d, J = 10.4, H-6''), 3.39 (1H, m, H-3'''), 3.28 (1H, m, H-2'''), 3.27 (1H, m, H-5'''), 3.24 (1H, m, H-3''), 3.22 (1H, m, H-2''), 3.22 (1H, m, H-5''), 3.07 (1H, m, H-4'''), 3.05 (1H, m, H-4''), 0.99 (3H, d, J = 6.4, H-6'''). <sup>13</sup>C NMR (175 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 176.9 (C-4), 161.1 (C-5), 160.4 (C-7), 160.0 (C-4'), 156.8 (C-9), 156.4 (C-2), 133.3 (C-3), 130.7 (C-2', 6'), 120.9 (C-1'), 115.1 (C-3', 5'), 103.1 (C-10), 101.6 (C-1''), 100.6 (C-1'''), 99.4 (C-6), 93.8 (C-8), 76.4 (C-5''), 75.8 (C-3''), 74.0 (C-2''), 71.3 (C-4'''), 70.5 (C-2'''), 70.3 (C-3'''), 69.9 (C-4''), 68.1 (C-5'''), 66.8 (C-6''), 17.6 (C-6''') [6].

**Kaempferol 3-O-neohesperidoside (2)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data. <sup>1</sup>H NMR (700 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm, J/Hz): 12.48 (1H, br.s, 5-OH), 8.03 (2H, d, J = 8.7, H-2', 6'), 6.85 (2H, d, J = 8.7, H-3', 5'), 6.30 (1H, br.s, H-8), 6.09 (1H, br.s, H-6), 5.42 (1H, d, J = 7.5, H-1''), 4.42 (1H, d, J = 1.2, H-1'''), 3.72 (1H, m, H-2'''), 3.71 (1H, m, H-5'''), 3.53 (1H, m, H-6''), 3.46 (1H, m, H-3'''), 3.42 (1H, m, H-2''), 3.37 (1H, m, H-3''), 3.27 (1H, m, H-6''), 3.12 (1H, m, H-4'''), 3.08 (1H, m, H-4''), 3.07 (1H, m, H-5''), 1.06 (3H, d, J = 6.25, H-6'''). <sup>13</sup>C NMR (175 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 176.9 (C-4), 161.1 (C-5), 160.4 (C-7), 160.0 (C-4'), 156.8 (C-9), 156.3 (C-2), 133.2 (C-3), 130.7 (C-2', 6'), 120.9 (C-1'), 115.1 (C-3', 5'), 103.1 (C-10), 101.9 (C-1''), 99.8 (C-1'''), 99.4 (C-6), 93.8 (C-8), 78.0 (C-2''), 77.7 (C-3''), 77.1 (C-5''), 71.9 (C-4'''), 70.6 (C-3'''), 70.2 (C-2'''), 69.7 (C-4''), 68.3 (C-5'''), 61.0 (C-6''), 17.5 (C-6''') [7].

**Isorhamnetin 3-O-rutinoside (3)**, light-yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data. <sup>1</sup>H NMR (700 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm, J/Hz): 12.48 (1H, br.s, 5-OH), 7.99 (1H, d, J = 2.3, H-2'), 7.49 (1H, dd, J = 8.8, 2.3, H-6'), 6.89 (1H, d, J = 8.8, H-5'), 6.32 (1H, br.s, H-8), 6.10 (1H, br.s, H-6), 5.42 (1H, d, J = 7.8, H-1''), 4.42 (1H, d, J = 0.94, H-1'''), 3.85 (3H, s, OCH<sub>3</sub>), 3.71 (2H, d, J = 10.4, H-6''), 3.38 (1H, m, H-3'''), 3.28 (1H, m, H-2'''), 3.26 (1H, m, H-5'''), 3.24 (1H, m, H-3''), 3.22 (1H, m, H-2''), 3.21 (1H, m, H-5''), 3.07 (1H, m, H-4'''), 3.05 (1H, m, H-4''), 1.04 (3H, d, J = 6.0, H-6'''). <sup>13</sup>C NMR (175 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 176.9 (C-4), 161.1 (C-5), 160.4 (C-7), 159.9 (C-4'), 156.8 (C-9), 156.5 (C-2), 147.2 (C-3'), 133.0 (C-3), 121.8 (C-6'), 120.8 (C-1'), 114.7 (C-5'), 113.0 (C-2'), 103.1 (C-10), 101.9 (C-1''), 99.9 (C-1'''), 99.4 (C-6), 93.8 (C-8), 76.4 (C-5''), 75.8 (C-3''), 74.0 (C-2''), 71.3 (C-4'''), 70.5 (C-2'''), 70.2 (C-3'''), 69.8 (C-4''), 68.1 (C-5'''), 66.8 (C-6''), 55.8 (OCH<sub>3</sub>), 17.7 (C-6''') [1].

**Quercetin 3-O- $\beta$ -D-glucopyranoside (hirsutrin) (4)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm, J/Hz): 12.63 (1H, s, 5-OH), 7.58 (1H, d, J = 2.3, H-2'), 7.57 (1H, dd, J = 9.0, 2.3, H-6'), 6.84 (1H, d, J = 9.0, H-5'), 6.40 (1H, d, J = 2.0, H-8), 6.20 (1H, d, J = 2.0, H-6), 5.46 (1H, d, J = 7.5, H-1''), 3.57 (2H, d, J = 11.0, H-6''), 3.39 (1H, m, H-5''), 3.23 (2H, m, H-2'', 3''), 3.10 (1H, m, H-4''). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 177.5 (C-4), 164.2 (C-7), 161.3 (C-5), 156.4 (C-9), 156.3 (C-2), 148.5 (C-3'), 144.9 (C-4'), 133.4 (C-3), 121.6 (C-6'), 121.2 (C-1'), 116.3 (C-2'), 115.3 (C-5'), 104.0 (C-10), 100.9 (C-1''), 98.7 (C-6), 93.5 (C-8), 77.6 (C-5''), 76.6 (C-3''), 73.2 (C-2''), 70.0 (C-4''), 61.0 (C-6'') [8, 10].

**Morin 3-O- $\beta$ -D-glucopyranoside (5)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm, J/Hz): 12.62 (1H, s, 5-OH), 7.53 (1H, d, J = 2.2, H-3'), 7.66 (1H, dd, J = 8.5, 2.3, H-5'), 6.82 (1H, d, J = 8.5, H-6'), 6.40 (1H, d, J = 2.0, H-8), 6.20 (1H, d, J = 2.0, H-6), 5.36 (1H, d, J = 7.7, H-1''), 3.56 (2H, m, H-6'').  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 177.5 (C-4), 164.2 (C-7), 161.3 (C-5), 156.4 (C-9), 156.2 (C-2), 148.5 (C-4'), 144.9 (C-2'), 133.5 (C-3), 122.1 (C-5'), 121.15 (C-1'), 121.5 (C-6'), 116.0 (C-3'), 104.0 (C-10), 101.9 (C-1''), 98.7 (C-6), 93.5 (C-8), 77.6 (C-5''), 76.6 (C-3''), 73.2 (C-2''), 70.0 (C-4''), 61.0 (C-6'') [9].

**Quercetin 3-O-rutinoside (6)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm, J/Hz): 12.58 (1H, s, 5-OH), 7.52 (1H, dd, J = 8.4, 1.9, H-6'), 7.50 (1H, d, J = 1.9, H-2'), 6.80 (1H, d, J = 8.4, H-5'), 6.38 (1H, br.s, H-8), 6.19 (1H, br.s, H-6), 5.34 (1H, d, J = 7.5, H-1''), 4.38 (1H, d, J = 1.1, H-1'''), 3.97 (1H, dd, J = 12.1, 3.9, H-6''), 3.63 (1H, dd, J = 12.1, 5.9, H-6''), 3.39 (1H, m, H-3'''), 3.28 (1H, m, H-2'''), 3.27 (1H, m, H-5'''), 3.24 (1H, m, H-3''), 3.22 (2H, m, H-2'', 5''), 3.07 (1H, m, H-4'''), 3.05 (1H, m, H-4''), 1.06 (3H, d, J = 6.9, H-6'').  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 177.4 (C-4), 164.2 (C-7), 161.3 (C-5), 156.7 (C-9), 156.4 (C-2), 148.5 (C-4'), 144.9 (C-3'), 133.3 (C-3), 121.6 (C-1'), 121.6 (C-6'), 116.1 (C-2'), 115.2 (C-5'), 103.9 (C-10), 101.2 (C-1''), 100.7 (C-1'''), 98.8 (C-6), 93.5 (C-8), 76.6 (C-3''), 76.0 (C-5''), 74.1 (C-2''), 71.9 (C-4'''), 70.6 (C-4''), 70.4 (C-2'''), 70.0 (C-3'''), 68.2 (C-5'''), 67.0 (C-6''), 17.9 (C-6''') [6, 11].

**Morin 3-O-rutinoside (7)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data. Table 2 gives the NMR spectral data.

**Quercetin 3-O-(2-O- $\alpha$ -L-rhamnopyranosyl)- $\beta$ -D-galactopyranoside (8)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm, J/Hz): 12.59 (1H, s, 5-OH), 7.72 (1H, dd, J = 8.4, 2.1, H-6'), 7.48 (1H, d, J = 2.1, H-2'), 6.80 (1H, d, J = 8.4, H-5'), 6.38 (1H, d, J = 2.1, H-8), 6.19 (1H, d, J = 2.1, H-6), 5.63 (1H, d, J = 7.8, H-1''), 5.06 (1H, br.s, H-1'''), 3.80 (1H, m, H-5''), 3.79 (1H, m, H-2''), 3.75 (1H, m, H-5'''), 3.73 (1H, m, H-3'''), 3.63 (1H, m, H-4''), 3.57 (1H, m, H-3''), 3.47 (1H, m, H-2'''), 3.42 (1H, m, H-6''), 3.27 (1H, m, H-6''), 3.12 (1H, m, H-4'''), 0.77 (3H, d, J = 6.1, H-6''').  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 177.4 (C-4), 164.2 (C-7), 161.3 (C-5), 156.6 (C-2), 156.4 (C-9), 148.1 (C-4'), 144.8 (C-3'), 133.4 (C-3), 122.3 (C-6'), 121.0 (C-1'), 115.7 (C-2'), 115.2 (C-5'), 104.0 (C-10), 100.5 (C-1'''), 98.8 (C-1''), 98.7 (C-6), 93.6 (C-8), 75.0 (C-2''), 75.0 (C-5''), 74.1 (C-3''), 71.9 (C-4'''), 70.7 (C-3'''), 70.6 (C-2'''), 68.6 (C-4''), 68.2 (C-5'''), 60.0 (C-6'), 17.2 (C-6''') [17].

**Morin 3-O-(2-O- $\alpha$ -L-rhamnopyranosyl)- $\beta$ -D-galactopyranoside (9)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data. Table 2 gives the NMR spectral data.

**Quercetin 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-[ $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-galactopyranoside (10)**, yellow amorphous compound. Table 1 gives the composition and UV and mass spectral data.  $^1\text{H}$  NMR (700 MHz, DMSO- $d_6$ ,  $\delta$ , ppm, J/Hz): 12.69 (1H, s, 5-OH), 7.67 (1H, dd, J = 8.4, 2.0, H-6'), 7.47 (1H, d, J = 2.0, H-2'), 6.79 (1H, d, J = 8.4, H-5'), 6.32 (1H, br.s, H-8), 6.12 (1H, br.s, H-6), 5.57 (1H, d, J = 7.8, H-1''), 5.05 (1H, br.s, H-1'''), 4.38 (1H, br.s, H-1'''), 3.80 (1H, m, H-2''), 3.73 (1H, m, H-2'''), 3.60 (1H, m, H-3''), 3.59 (1H, m, H-4''), 3.57 (2H, m, H-6''), 3.56 (1H, m, H-5''), 3.49 (1H, m, H-3'''), 3.38 (1H, m, H-2'''), 3.37 (1H, m, H-5'''), 3.35 (1H, m, H-5'''), 3.29 (1H, m, H-3'''), 3.12 (2H, m, H-4''', 4'''), 1.05 (3H, d, J = 6.1, H-6'''), 0.80 (3H, d, J = 6.1, H-6''').  $^{13}\text{C}$  NMR (175 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 177.0 (C-4), 164.8 (C-7), 161.3 (C-5), 156.4 (C-9), 156.1 (C-2), 148.6 (C-3'), 144.9 (C-4'), 132.8 (C-3), 122.1 (C-6'), 121.1 (C-1'), 115.6 (C-2'), 115.2 (C-5'), 103.5 (C-10), 100.6 (C-1''), 100.1 (C-1'''), 99.1 (C-1'), 99.0 (C-6), 93.7 (C-8), 74.9 (C-2''), 73.9 (C-3''), 73.2 (C-5''), 71.97 (C-4''', 4'''), 70.8 (C-2'''), 70.7 (C-3''', 3'''), 70.5 (C-2'''), 68.6 (C-4''), 68.4 (C-5'''), 68.2 (C-5'''), 65.0 (C-6'), 17.9 (C-6'''), 17.3 (C-6''') [18].

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