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NEW COMPOUNDS FROM FLOWERS OF *Phlojodicarpus sibiricus*

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Chromatographic separation of the MeOH extract from flowers of Phlojodicarpus sibiricus *(Fisch.) Koso.-Pol. (Apiaceae) isolated 27 compounds including three new glycosides, the structures of which were established by UV, IR, and NMR spectroscopy and mass spectrometry as (*R*)-peucedanol -7-*O*-(6″-*O*-β-*D*-apiofuranosyl)-β-*D*-glucopyranoside-3′-*O*-β-*D*-glucopyranoside (phlojosibiriside I,* ***1****), diosmetin-7-*O*-(6″-*O*-β-*D*-apiofuranosyl)-β-*D*-glucopyranoside (phlojosibiriside II,* ***2****), and diosmetin-7-*O*-(2″-*O*-acetyl-6″-*O*-β-*D*- apiofuranosyl)-β-*D*-glucopyranoside (phlojosibiriside III,* ***3****).*

Keywords: *Phlojodicarpus sibiricus*, Apiaceae, *phlojosibiriside, peucedanol, diosmetin*.

Phlojodicarpus Turcz. ex Ledeb. is a small genus of medicinal plants in the family Apiaceae, representatives of which are distributed in Siberia, the Russian Far East, and Mongolia [1]. The species *P. sibiricus* (Fisch.) Koso.-Pol. is used most in eastern Siberia to treat atherosclerosis, obesity, tuberculosis, and stomach diseases [2]. Information on the chemical composition of *P. sibiricus* indicates the presence in it of simple coumarins and their glycosides, khellactone esters, hydroxycinnamates, flavonoids, and essential oil [1, 3–5]. Only roots, herb, or seeds of *P. sibiricus* have been chemically analyzed because of their wide use as medicinal raw material. Information on the compounds extracted from flowers of this species is missing, which hinders drawing a conclusion about their possible practical value. In continuation of studies of Siberian species of *Phlojodicarpus* [1, 6], the composition of phenolic compounds from flowers of *P. sibiricus* were studied in the present work.

Chromatographic separation of the MeOH extract from *P. sibiricus* flowers by column chromatography (CC) over silica gel, polyamide, and Sephadex LH-20 and by preparative HPLC isolated three new glycosides **1**–**3** and 24 known compounds (**4**–**27**) that were identified using UV, IR, and NMR spectroscopy and mass spectrometry as 3′,4′-di-*O*-isobutyryl-*cis*-khellactone (**4**) [7], praeruptorin D (**5**) [8], dihydrosamidin (**6**) [9], visnadin (**7**) [10], hyuganin D (**8**) [11], 3′,4′-di-*O*-acetyl-*cis*-khellactone (**9**) [12], 4′-*O*-acetyl-*cis*-khellactone (**10**) [13], praeroside II (**11**) [14], praeroside VI (**12**) [14], diosmetin-7-*O*-glucoside (**13**) [15], (*R*)-peucedanol-7-*O*-glucoside (**14**) [16], (*R*)-peucedanol-2′-*O*-glucoside (**15**) [16], (*R*)-peucedanol-3′-*O*-glucoside (**16**) [16], skimmin (**17**) [17], umbelliferone-7-*O*-(6″-apiosyl)glucoside (**18**) [5], 4,5-di-*O*-caffeylquinic acid (**19**) [18], 3,5-di-*O*-caffeoylquinic acid (**20**) [19], 1,3-di-*O*-caffeoylquinic acid (**21**) [18], 5-*O*-caffeoylquinic acid (**22**) [20], 4-*O*-caffeoylquinic acid (**23**) [18], 1-*O*-caffeoylquinic acid (**24**) [18], peujaponiside (**25**) [21], (*R*)-peucedanol-2′-*O*-(6″-apiosyl)glucosides (**26**) [22], and (*R*)-peucedanol-3′-*O*-(6″-apiosyl)glucoside (**27**) [23]. Compounds **5**–**10**, **14**, **16**, **18**, **22**, and **24** were previously observed in *P. sibiricus* [1, 3–5]; constituents **4**, **11**–**13**, **15**, **17**, **19**–**21**, **23** and **25**–**27** were detected for the first time for this species.

Compound **1** had the molecular formula $C_{31}H_{44}O_{19}$ based on HR-ESI-MS (*m*/*z* 721.4007 $[M + H]^+$; calcd 721.6296) and ^{13}C NMR data (Table 1). The UV spectrum was similar to those of 7-hydroxycoumarins (λ_{max} 249, 289sh, 330 nm) [21]. The IR spectrum contained bands for carbonyl (1708 cm^{-1}) and an aromatic ring (1625) that were characteristic of coumarins [16]. The acid-hydrolysis products of **1** included D-glucose and D-apiose in a 2:1 ratio and (*R*)-peucedanol, which was identified using $[\alpha]_D$, UV and NMR spectroscopy, and mass spectrometry as compared to the known compound and literature data [24]. The positive-ion mass spectrum had peaks for the protonated molecule (*m*/*z* 721 $[M + H]^+$) and adduct ions (*m*/*z* 743 $[M + Na]^+$ and 759 $[M + K]^+$) and peaks caused by loss of two glucoses (162 amu; $C_6H_{10}O_5$) and one apiose (132 amu; $C_5H_8O_4$) with *m*/*z* 589, 559, 427, and 265 [1].

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TABLE 1. ^{13}C NMR Spectra of **1**–**3** (125 MHz, MeOH-d_4, 298 K, δ, ppm)

C atom	1	2	3	C atom	1	2	3
2	164.5	164.4	164.2	2″	75.2	74.8	76.5
3	114.1	103.2	103.4	3″	77.9	77.6	75.4
4	146.9	182.2	182.4	4″	71.7	71.6	71.5
5	131.6	161.2	160.8	5″	78.3	78.5	78.2
6	128.3	100.3	100.1	6″	69.8	70.1	69.8
7	160.4	163.1	163.4	2″-$\underline{C}H_3CO$	–	–	21.4
8	104.4	95.1	95.3	2″-$CH_3\underline{C}O$	–	–	171.2
9	155.8	157.8	157.7	1‴	110.5	110.2	110.4
10	114.9	105.2	105.7	2‴	76.9	76.7	76.8
1′	32.9	122.0	121.7	3‴	80.5	80.6	80.2
2′	78.8	110.6	111.9	4‴	75.7	75.4	75.2
3′	82.1	146.3	146.5	5‴	65.2	65.4	65.3
4′	–	150.7	150.5	1⁗	100.4	–	–
5′	–	114.7	114.4	2⁗	74.8	–	–
6′	–	120.2	119.8	3⁗	77.5	–	–
3′,3′-$(CH_3)_2$	23.2, 23.7	–	–	4⁗	71.4	–	–
4′-OCH_3	–	59.1	58.7	5⁗	78.0	–	–
1″	102.5	102.1	100.2	6⁗	62.1	–	–

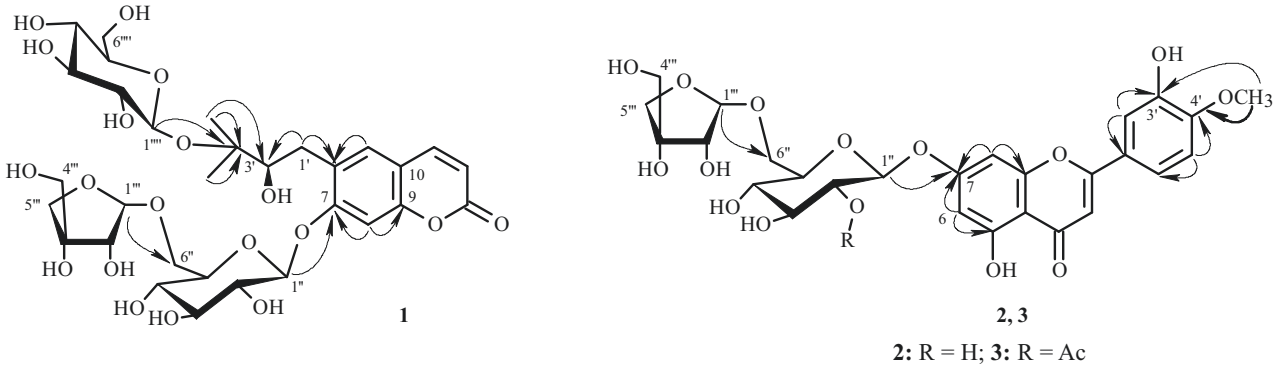

Fig. 1. Structures and HMBC correlations of **1**–**3**.

The positions of resonances in PMR and ^{13}C NMR spectra were close to those of the known glycoside (*R*)-peucedanol-3′-*O*-(6″-apiosylfuranosyl)glucopyranoside (**26**) [23] besides additional resonances due to the additional glucose residue. The PMR spectrum had two doublets at δ 6.31 and 7.81 (J = 9.2 Hz, H-3 and H-4) and two singlets for aromatic protons at δ 7.43 and 6.94 (H-5 and H-8), which were typical for 7-hydroxy-6-substituted coumarins [21]. Two paired doublets at δ 2.48 and 3.02 (H-1′$_a$ and H-1′$_b$) and two 3H singlets at δ 1.22 and 1.25 (H-3′) were attributed to the 3,4-dihydroxyisopentyl side chain on C-6 of (*R*)-peucedanol [16]. The SSCCs for the anomeric proton resonances of glucopyranoses (δ 4.96/4.69) and apiofuranoses of **1** and **2** (δ 5.63) of 7.1/7.6 and 2.5 Hz, respectively, were consistent with their β-configurations [16]. HMBC spectral data (Fig. 1) allowed the attachment sites of the carbohydrates to the aglycon to be found. Several key correlations were observed between resonances for glucopyranose H-1″ of **1** (δ 4.96) and aglycon C-7 (δ 160.4); apiofuranose H-1‴ (δ 5.63) and glucopyranose C-6″ of **1** (δ 69.8); glucopyranose H-1⁗ of **2** (δ 4.69) and side-chain C-3′ (δ 82.1). Thus, the 6″-*O*-β-D-apiofuranosyl-β-D-glucopyranose was bonded to C-7 of (*R*)-peucedanol; β-D-glucopyranose, to side-chain C-3′. The studies established the structure of **1** as (*R*)-peucedanol-7-*O*-(6″-*O*-β-D-apiofuranosyl)-β-D-glucopyranoside-3′-*O*-β-D-glucopyranoside, which was called phlojosibiriside I. Several monoglycosides of (*R*)-peucedanol are known and include the 7-*O*-, 2′-*O*-, and 3′-*O*-monoglucosides from *Seseli montanum* L. [16] and the 3′-*O*-(6″-apiosyl)glucoside from *Peucedanum japonicum* Thunb. [21], *Phlojodicarpus villosus* (Turcz. ex Fisch. & C. A. Mey.) Turcz. ex Ledeb., and *P. sibiricus* [23]. The (*R*)-peucedanol diglycoside was observed for the first time in nature.

Compound **2** had the molecular formula $C_{27}H_{30}O_{15}$ according to HR-ESI-MS (*m/z* 593.6384 $[M - H]^-$; calcd 593.4704) and ^{13}C NMR spectroscopy. The UV spectrum showed bands typical of flavones (λ_{max} 255, 270, 344 nm) [25]. Hydrolysis of **2** produced D-glucose and D-apiose 1:1) and diosmetin [26]. The negative-ion mass spectrum contained peaks for the deprotonated molecule with *m/z* 593 $[M - H]^-$ and ions with *m/z* 461 and 299 due to sequential loss of apiose and glucose, respectively. The positions of resonances in PMR and ^{13}C NMR spectra were close to those of diosmetin-7-*O*-*β*-D-glucopyranoside (**13**) [15] although with additional resonances for apiofuranose at δ 5.59 (H-1‴), 3.79 (H-2‴), 3.70, 4.30 (H-4‴), and 3.67 (H-5‴) in the PMR spectrum and at δ 110.2 (C-1‴), 76.7 (C-2‴), 80.6 (C-3‴), 75.4 (C-4‴), and 65.4 (C-5‴) in the ^{13}C NMR spectrum. The SSCCs for resonances of the glucopyranose (J = 7.4 Hz) and apiofuranose anomeric protons (J = 2.2 Hz) were consistent with their *β*-configurations. The weak-field shift of the glucopyranose C-6″ resonance (δ_C 61.5→70.1) relative to **13** indicated the presence of a substituent that was an apiofuranose according to the HMBC spectrum (Fig. 1) because correlations were found between apiose H-1‴ (δ 5.59) and glucose C-6″ (δ 70.1). The results indicated that **2** was diosmetin-7-*O*-(6″-*O*-*β*-apiofuranosyl)-*β*-D-glucopyranoside and was called phlojosibiriside II.

The molecular mass of **3** was 42 amu greater ($C_{29}H_{32}O_{16}$, *m/z* 635.3718 $[M - H]^-$) than that of **2**. Its spectral characteristics were similar to those of **2**. Results from mass spectrometry {*m/z* 635 $[M - H]^-$, 593 $[(M - H) - C_2H_2O]^-$} and PMR (δ 1.90, 3H, s) and ^{13}C NMR spectroscopy [δ 21.4 ($\underline{C}H_3CO$), 171.2 ($CH_3\underline{C}O$)] indicated that an additional acetyl was present in **3** [27, 28]. The acetyl was confirmed to be located on C-2″ because the glucopyranose C-2″ resonance was shifted to weak field (δ_C 74.8→76.5) as compared to **2** and correlations were observed between the acetyl protons (δ_H 1.90) and glucopyranose C-2″ (δ_C 76.5) in the HMBC spectrum. These results allowed **3** to be described as an acetyl derivative of phlojosibiriside II or diosmetin-7-*O*-(2″-*O*-acetyl-6″-*O*-*β*-D-apiofuranosyl)-*β*-D-glucopyranoside, which was called phlojosibiriside III.

Information on diosmetin apioglycosides is scant. The only known compound is diosmetin-7-*O*-(2″-*O*-apiosyl-6″-*O*-acetyl)glucoside from *Paullinia pinnata* L. (Sapindaceae) [28], an isomer of which is phlojosibiriside III. It was shown earlier that 6″-*O*-apiosylglucose could be incorporated in phenolic compounds observed in *Phlojodicarpus* species. In particular, umbelliferone 6″-*O*-apiosylglucoside (**18**) was also found in *P. villosus* and *P. turczaninovii* Sipliv. [*Ferulopsis hystrix* (Bunge) Pimenov] [1, 5]. The incorporation of apiose into phenolic glycosides is probably a chemical signature of the genus *Phlojodicarpus*.

In general, the research showed that the composition of phenolic compounds from *P. sibiricus* was similar to that of other organs (roots, herb, seeds) [1, 5] but differed by a larger structural variety of coumarin and flavonoid glycosides, which allowed flowers of *P. sibiricus* to be considered medicinal raw material.

EXPERIMENTAL

General comments were published [1, 32]. Flowers of *P. sibiricus* were collected in Barguzinsky District (Republic of Buryatia, Russia; July 26, 2016; 53°59′26.3″ N, 108°89′17.2″ E). A specimen of the raw material is preserved at the herbarium of the IGEB, SB, RAS (No. CRo/an-03/23-25/0716). The species was determined by Dr. T. A. Aseeva (IGEB, SB, RAS). Raw material was dried in a convection oven (50°C) to moisture <5% and ground (1–2 mm).

Isolation of 1–26. Plant raw material (860 g) was extracted (3×) with MeOH (1:12, 50°C) in an ultrasonic bath (100 W, 35 Hz). The extract was concentrated to dryness and suspended in H_2O (1:5). The resulting suspension was extracted with hexane, EtOAc, and BuOH to give fractions P-1 (34.4 g), P-2 (80.8), and P-3 (120.4), respectively. Fraction P-1 (30 g) was chromatographed over SiO_2 (CC, 50 × 5 cm, eluent hexane–EtOAc, 100:0→50:50), RP-SiO_2 (CC, 40 × 2 cm, eluent H_2O–MeCN, 50:50→0:100), and Sephadex LH-20 (CC, 50 × 1 cm, eluent MeCN–Me_2CO, 100:0→80:20) and by preparative (prep.) HPLC [isocratic (% MeCN): 0–90 min, 80%] to afford 3′,4′-di-*O*-isobutyryl-*cis*-khellactone (14 mg, **4**) [7], 3′,4′-di-*O*-angeloyl-*cis*-khellactone (praeruptorin D, 19 mg, **5**) [8], 3′-*O*-isovaleryl-4′-*O*-acetyl-*cis*-khellactone (dihydrosamidin, 821 mg, **6**) [8, 9], 3′-*O*-(2″-methylbutyryl)-4′-*O*-acetyl-*cis*-khellactone (visnadin, 15 mg, **7**) [10], 3′-*O*-acetyl-4′-*O*-isobutyryl-*cis*-khellactone (hyuganin D, 215 mg, **8**) [11], 3′,4′-di-*O*-acetyl-*cis*-khellactone (11 mg, **9**) [12], and 4′-*O*-acetyl-*cis*-khellactone (20 mg, **10**) [13].

Fraction P-2 (75 g) was separated by CC over polyamide (30 × 6 cm, eluent H_2O–EtOH, 100:0→10:90), SiO_2 (CC, 20 × 3 cm, eluent hexane–EtOAc, 100:0→70:30), RP-SiO_2 (CC, 40 × 2 cm, eluent H_2O–MeCN, 100:0→30:70), and Sephadex LH-20 (CC, 50 × 1 cm, eluent EtOH–H_2O, 90:10→30:70) and by prep. HPLC [gradient mode (% MeCN): 0–70 min, 5–50%, 50–90 min, 50–80%] to isolate **1** (27 mg), *cis*-khellactone-3′-*O*-glucoside (praeroside II, 38 mg, **11**) [14], *cis*-khellactone-3′-

O-(6″-apioside)glucoside (praeroside VI, 26 mg, **12**) [14], diosmetin-7-*O*-glucoside (41 mg, **13**) [15], (*R*)-peucedanol-7-*O*-glucoside (21 mg, **14**) [16], (*R*)-peucedanol-2′-*O*-glucoside (11 mg, **15**) [16], (*R*)-peucedanol-3′-*O*-glucoside (9 mg, **16**) [16], umbelliferone-7-*O*-glucoside (skimmin, 57 mg, **17**) [17], umbelliferone-7-*O*-(6″-apiosyl)glucoside (43 mg, **18**) [5], 4,5-di-*O*-caffeoylquinic acid (37 mg, **19**) [18], 3,5-di-*O*-caffeoylquinic acid (42 mg, **20**) [19], 1,3-di-*O*-caffeoylquinic acid (51 mg, **21**) [18], 5-*O*-caffeoylquinic acid (308 mg, **22**) [20], 4-*O*-caffeoylquinic acid (9 mg, **23**) [18], and 1-*O*-caffeoylquinic acid (5 mg, **24**) [18].

Chromatographic separation of fraction P-3 (95 g) over polyamide (50 × 6 cm, eluent H_2O–EtOH, 100:0→10:90) and Sephadex LH-20 (CC, 50 × 1 cm, eluent EtOH–H_2O, 90:10→10:90) and by prep. HPLC [gradient mode (% MeCN): 0–50 min, 5–30%, 50–70 min, 30–40%, 70–90 min, 40–65%] to afford **2** (31 mg), **3** (18 mg), (*R*)-peucedanol-7-*O*-(6″-apiosyl)glucoside (peujaponiside, 24 mg, **25**) [21], (*R*)-peucedanol-2′-*O*-(6″-apiosyl)glucoside (10 mg, **26**) [22], and (*R*)-peucedanol-3′-*O*-(6″-apiosyl)glucoside (14 mg, **27**) [23].

Phlojosibiriside I (1). $C_{31}H_{44}O_{19}$. UV spectrum (50% EtOH, λ_{max}, nm): 249, 289 sh, 330. IR spectrum (ν, cm^{-1}): 1625, 1708. HR-ESI-MS, *m/z* 721.4007 $[M + H]^+$ (calcd 721.6296); (+)ESI-MS, *m/z*: 721 $[M + H]^+$, 743 $[M + Na]^+$, 759 $[M + K]^+$; 721→559 $[(M + H) – C_6H_{10}O_5]^+$, 589 $[(M + H) – C_5H_8O_4]^+$; 559→427 $[(M + H) – C_6H_{10}O_5 – C_5H_8O_4]^+$, 265 $[(M + H) – 2 \times C_6H_{10}O_5 – C_5H_8O_4]^+$; (–)ESI-MS, *m/z*: 719 $[M – H]^–$, 263 $[(M – H) – 2 \times C_6H_{10}O_5 – C_5H_8O_4]^–$. ^{1}H NMR spectrum (500 MHz, MeOH-d_4, 298 K, δ, ppm, J/Hz): aglycon – 7.81 (1H, d, J = 9.2, H-4), 7.43 (1H, s, H-5), 6.94 (1H, s, H-8), 6.31 (1H, d, J = 9.2, H-3), 4.06 (1H, dd, J = 9.8, 1.7, H-2′), 3.02 (1H, dd, J = 14.0, 1.7, H-1′$_b$), 2.48 (1H, dd, J = 14.0, 10.1, H-1′$_a$), 1.22, 1.25 (2 × 3H, s, 3′,3′-$(CH_3)_2$); 7-*O*-β-*D*-glucopyranose – 4.96 (1H, d, J = 7.1, H-1″), 4.15 (1H, m, H-6″$_a$), 3.60 (1H, m, H-6″$_b$), 3.10–3.58 (8H, m, H-2″–5″, H-2‴–5‴); 6″-*O*-β-*D*-apiofuranose – 5.63 (1H, d, J = 2.5, H-1‴), 4.29 (1H, m, H-4‴$_b$), 4.01 (1H, m, H-6‴$_a$), 3.78 (1H, m, H-2‴), 3.72 (1H, m, H-4‴$_a$), 3.65 (2H, m, H-5‴); 3′-*O*-β-*D*-glucopyranose – 4.69 (1H, d, J = 7.6, H-1⁗), 3.70 (1H, m, H-6⁗$_b$), 3.10–3.58 (8H, m, H-2″–5″, H-2⁗–5⁗). ^{13}C NMR spectrum (125 MHz, MeOH-d_4, 298 K, δ, ppm) is given in Table 1.

(*R*)-Peucedanol. $C_{14}H_{16}O_5$. $[\alpha]_D^{20}$ +48.9° (*c* 1.0, EtOH) {lit.: $[\alpha]_D^{23}$ +43.3° (*c* 1.2, EtOH) [21]}. UV spectrum (50% EtOH, λ_{max}, nm): 248, 258, 290 sh, 333. HR-ESI-MS, *m/z*: 265.4711 $[M + H]^+$ (calcd 265.2620); (+)ESI-MS, *m/z*: 265 $[M + H]^+$, 287 $[M + Na]^+$, 303 $[M + K]^+$; (–)ESI-MS, *m/z*: 263 $[M – H]^–$. ^{1}H NMR spectrum (500 MHz, MeOH-d_4, 298 K, δ, ppm, J/Hz): 7.86 (1H, d, J = 9.1, H-4), 7.45 (1H, s, H-5), 6.90 (1H, s, H-8), 6.30 (1H, d, J = 9.1, H-3), 3.67 (1H, dd, J = 10.1, 2.0, H-2′), 2.94 (1H, dd, J = 14.1, 2.0, H-1′$_b$), 2.33 (1H, dd, J = 14.1, 10.0, H-1′$_a$), 1.21, 1.23 (2 × 3H, s, 3′,3′-$(CH_3)_2$). ^{13}C NMR spectrum (125 MHz, MeOH-d_4, 298 K, δ, ppm): 164.3 (C-2), 112.0 (C-3), 147.2 (C-4), 131.9 (C-5), 126.9 (C-6), 161.7 (C-7), 103.1 (C-8), 156.1 (C-9), 112.9 (C-10), 32.8 (C-1′), 79.2 (C-2′), 74.3 (C-3′), 25.5, 26.1 {3′,3′-$(\underline{C}H_3)_2$}.

Phlojosibiriside II (2). $C_{27}H_{30}O_{15}$. UV spectrum (50% EtOH, λ_{max}, nm): 255, 270, 344. HR-ESI-MS, *m/z*: 593.6384 $[M – H]^–$ (calcd 593.4704). (+)ESI-MS, *m/z*: 595 $[M+H]^+$; (–)ESI-MS, *m/z*: 593 $[M – H]^–$; 593→461 $[(M – H) – C_5H_8O_4]^–$, 299 $[(M – H) – C_5H_8O_4 – C_6H_{10}O_5]^–$; 299→285 $[(M – H) – C_5H_8O_4 – C_6H_{10}O_5 – CH_2]^–$. ^{1}H NMR spectrum (500 MHz, MeOH-d_4/DMSO-d_6*, 298 K, δ, ppm, J/Hz): aglycon – 13.04* (1H, br.s, 5-OH), 9.84* (1H, br.s, 3′-OH), 7.76 (1H, dd, J = 2.0, 8.0, H-6′), 7.50 (1H, d, J = 2.2, H-2′), 7.04 (1H, d, J = 8.0, H-5′), 6.87 (1H, s, H-3), 6.78 (1H, d, J = 2.1, H-8), 6.43 (1H, d, J = 2.1, H-6), 3.82 (3H, s, 4′-OCH_3); 7-*O*-β-*D*-glucopyranose – 5.03 (1H, d, J = 7.4, H-1″), 4.07 (1H, m, H-6″$_a$), 3.64 (1H, m, H-6″$_b$), 3.37 (1H, m, H-2″), 3.07–3.31 (3H, m, H-3″–5″); 6″-*O*-β-*D*-apiofuranose – 5.59 (1H, d, J = 2.2, H-1‴), 4.30 (1H, m, H-4‴$_b$), 3.79 (1H, m, H-2‴), 3.70 (1H, m, H-4‴$_a$), 3.67 (2H, m, H-5‴). ^{13}C NMR spectrum (125 MHz, MeOH-d_4, 298 K, δ, ppm) is given in Table 1.

Phlojosibiriside III (3). $C_{29}H_{32}O_{16}$. UV spectrum (50% EtOH, λ_{max}, nm): 254, 270, 343. IR spectrum (ν, cm^{-1}): 1638, 1720. HR-ESI-MS, *m/z* 635.3718 $[M – H]^–$ (calcd 635.5042); (+)ESI-MS, *m/z* 637 $[M + H]^+$; (–)ESI-MS, *m/z*: 635 $[M – H]^–$; 635→593 $[(M – H) – C_2H_2O]^–$; 593→461 $[(M – H) – C_2H_2O – C_5H_8O_4]^–$, 299 $[(M – H) – C_2H_2O – C_5H_8O_4 – C_6H_{10}O_5]^–$; 299→285 $[(M – H) – C_2H_2O – C_5H_8O_4 – C_6H_{10}O_5 – CH_2]^–$. ^{1}H NMR spectrum (500 MHz, MeOH-d_4/DMSO-d_6*, 298 K, δ, ppm, J/Hz): aglycon – 13.01* (1H, br.s, 5-OH), 9.89* (1H, br.s, 3′-OH), 7.69 (1H, dd, J = 2.0, 8.3, H-6′), 7.43 (1H, d, J = 2.0, H-2′), 7.01 (1H, d, J = 8.3, H-5′), 6.75 (1H, s, H-3), 6.70 (1H, d, J = 2.0, H-8), 6.42 (1H, d, J = 2.0, H-6), 3.83 (3H, s, 4′-OCH_3); 7-*O*-β-*D*-glucopyranose – 4.98 (1H, d, J = 7.2, H-1″), 4.11 (1H, m, H-6″$_a$), 3.62 (1H, m, H-6″$_b$), 3.49 (1H, m, H-2″), 3.02–3.29 (3H, m, H-3″–5″), 1.90 (3H, s, 2″-CH_3CO); 6″-*O*-β-*D*-apiofuranose – 5.46 (1H, d, J = 2.1, H-1‴), 4.25 (1H, m, H-4‴$_b$), 3.82 (1H, m, H-2‴), 3.74 (1H, m, H-4‴$_a$), 3.69 (2H, m, H-5‴). ^{13}C NMR spectrum (125 MHz, MeOH-d_4, 298 K, δ, ppm) is given in Table 1.

Acid Hydrolysis. The compound (5–7 mg) and TFA (5%) in Me_2CO (70%, 3 mL) was heated at 110°C (60 min). The hydrolysate was concentrated to dryness under vacuum. The dry residue was dissolved in EtOH (50%, 5 mL).

The resulting solution was placed on polyamide (10 g) and eluted by H_2O (50 mL, eluate I) and MeOH (70%, 100 mL, eluate II). The monosaccharide composition in eluate I and their assignment as D- and L-types were determined by HPLC-UV after reaction with 3-methyl-1-phenyl-2-pyrazolin-5-one [29] and L-tryptophan [30], respectively. The aglycons were analyzed by HPLC-MS [31] using retention times and UV and mass spectra and comparisons with known compounds and literature data. Eluate I of **1** contained D-glucose and D-apiose (2:1); **2** and **3**, D-glucose and D-apiose (1:1). Eluate II of **1** contained (*R*)-peucedanol [16]; **2** and **3**, diosmetin [26].

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