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# RHAMNETIN GLYCOSIDES FROM THE GENUS *Spiraea*

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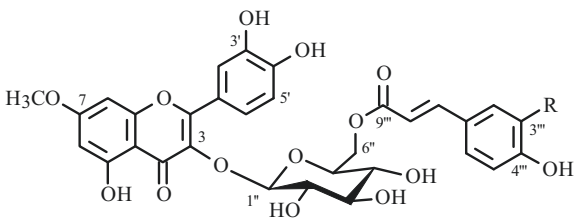
*Rhamnetin (7-*O*-methylquercetin, **1**) and its glycosides were found for the first time in the genus* Spiraea *(Rosaceae) during chromatographic studies of representatives from the subgenus* Protospiraea*. Leaves of* S. salicifolia *yielded **1**, rhamnetin-3-*O*-β-D-glucopyranoside (**2**), and two new flavonoids **3** and **4** that were identified by UV, IR, and NMR spectroscopy and mass spectrometry as rhamnetin-3-*O*-(6″-*O*-p-coumaroyl)-β-D-glucopyranoside (spiraearhamnin A, **3**) and rhamnetin-3-*O*-(6″-*O*-caffeoyl)-β-D-glucopyranoside (spiraearhamnin B, **4**). Leaves of* S. betulifolia *and* S. betulifolia *var.* aemiliana *afforded **1** and **2** and glycosides of kaempferol, quercetin, and isorhamnetin. Species of the subgenus* Metaspiraea *(*S. alpina*,* S. chamaedryfolia*,* S. dahurica*,* S. hypericifolia*, and* S. media*) did not contain **1** or its derivatives.*

**Keywords:** *Spiraea*, Rosaceae, rhamnetin-3-*O*-(6″-*O*-*p*-coumaroyl)-*β*-D-glucopyranoside, rhamnetin-3-*O*-(6″-*O*-caffeoyl)-*β*-D-glucopyranoside, spiraearhamnin, *Protospiraea*, *Metaspiraea*.

The genus *Spiraea* (Rosaceae) is an interesting subject for chemotaxonomic studies because of the broad distribution and various opinions about the number of species, which are complicated by hybridization and polymorphism. Flavonoids of various structural types are considered marker compounds for this genus and the family as a whole [1]. Characteristic flavonoids of the genus *Spiraea* are the flavonols kaempferol and quercetin and their glycosides [1], which were detected in *S. canescens* D. Don [2], *S. cantoniensis* Lour. [3], *S. chamaedryfolia* L. [4], *S. formosana* Hayata [5], *S. hypericifolia* L., *S. media* Schmidt [4], and *S. salicifolia* L. [6]. Methoxylated quercetin derivatives including rhamnazin and the dimeric flavonols sparin A and B, which were atypical of the genus, were relatively recently isolated from *S. brahuica* Boiss. [7]. Isorhamnetin was also observed in several Siberian *Spiraea* species [8]. This suggested that methoxylated flavonols were more broadly distributed within this genus.

Previously, the isolation of kaempferol and quercetin glycosides and their acylated derivatives from *S. salicifolia* was reported by us [9]. In continuation of research on *Spiraea* flavonoids, we detected traces of rhamnetin (7-*O*-methylquercetin) in the hydrolysate of leaves from *S. salicifolia*. Herein, results from studies of several *Spiraea* species for the presence of rhamnetin and its derivatives are presented.

Four compounds were isolated by chromatographic separation from the EtOAc fraction of *S. salicifolia* and were identified as rhamnetin (**1**), rhamnetin-3-*O*-*β*-D-glucopyranoside (**2**), and two new flavonoid glycosides **3** and **4**.




**3, 4**

**3:** R = H; **4:** R = OH

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Compound **3** had the formula $C_{31}H_{28}O_{14}$ according to HR-ESI-MS (625.218 $[M + H]^+$; calcd 625.591). The UV and IR spectra indicated that **3** was an acylated flavonoid glycoside [10]. The flavonoid aglycon **3a**, D-glucose, and *p*-coumaric acid were identified in its hydrolysis products. The ESI-$MS^2$ spectrum of **3a** showed two strong ions with *m*/*z* 317 and 302 that corresponded to the pseudomolecular ion $[M + H]^+$ and its demethylated fragment $[(M + H) – 15]^+$.

A comparison of its $^{13}C$ NMR spectrum with that of quercetin indicated that C-7 underwent a weak-field shift (δ 163.8→164.8) with C-6 (δ 98.2→97.3) and C-8 (δ 93.7→92.5) experiencing simultaneously strong-field shifts [11]. These features allowed **3a** to be characterized as rhamnetin (7-*O*-methylquercetin). HPLC analyses also confirmed that the retention times of **3a** and rhamnetin standard sample were similar and different from those of isorhamnetin (3′-*O*-methylquercetin) and tamarixetin (4′-*O*-methylquercetin). The ESI-MS of **3** gave peaks for a pseudomolecular ion $[M + H]^+$ with *m*/*z* 625 and fragments formed by sequential cleavage of *p*-coumaric acid (479) $[(M + H) –146]^+$ and glucopyranose (317) $[(M + H) – 146 – 162]^+$. This indicated that the probable structure was a rhamnetin glycoside with an acylated carbohydrate [12, 13].

The PMR and $^{13}C$ NMR spectra were similar to those of rhamnetin-3-*O*-β-D-glucopyranoside (**2**) (Table 1) [14]. Glycosylation of flavonoid C-3 was indicated by shifts of C-3 (δ 136.2→133.5) and C-2 (δ 147.5→157.2) as compared with those of rhamnetin (**3a**) and correlations in the HMBC spectrum between resonances for glucopyranose H-1″ (δ 5.44) and rhamnetin C-3 (δ 133.5) [15]. Additional resonances in the PMR spectrum were attributed to protons of a *trans* double bond [δ 6.28 (1H, d, J = 16.0) and 7.40 (1H, d, J = 16.0)] and a *para*-substituted benzene ring [δ 6.78 (2H, d, J = 9.0) and 7.92 (2H, d, J = 9.0)] in *p*-coumaric acid. Resonances of glucopyranose H-6″ (δ 4.45 and 4.63) and C-6″ (δ 64.1) were shifted to weak field, indicating that an acyl group added to carbohydrate C-6″. HMBC spectra in which correlations were observed between resonances of glucopyranose H-6″ (δ 4.45 and 4.63) and *p*-coumaric acid carbonyl C-9‴ (δ 166.5) confirmed this. The results determined the structure of **3** as rhamnetin-3-*O*-(6″-*O*-*p*-coumaroyl)-β-D-glucopyranoside, which was named spiraearhamnin A.

Compound **4** had the formula $C_{31}H_{28}O_{15}$ (HR-ESI-MS *m*/*z* 641.402 $[M + H]^+$; calcd 641.591). The hydrolysis products of **4** were rhamnetin, D-glucose, and caffeic acid. The ESI-MS spectrum gave a peak for the protonated ion with *m*/*z* 641 $[M + H]^+$ and peaks for fragments with *m*/*z* 479 and 317 due to sequential cleavage of caffeic acid and glucose [3]. A comparison of the PMR and $^{13}C$ NMR spectra showed that they were similar to those of **3** but differed in the positions of resonances from a 1,3,4-trisubstituted benzene ring including proton resonances at δ 7.12 (H-2‴), 6.80 (H-5‴), and 6.89 (H-6‴) and $^{13}C$ resonances at δ 127.0 (C-1‴), 115.0 (C-2‴), 146.5 (C-3‴), 148.0 (C-4‴), 116.5 (C-5‴), and 123.3 (C-6‴) [16]. Correlations in the HMBC spectrum between resonances of glucopyranose proton H-6″ (δ 4.40 and 4.69) and caffeic acid C-9‴ (δ 166.2) indicated that the latter was bonded to carbohydrate C-6″. Compound **4** was identified based on the results as rhamnetin-3-*O*-(6″-*O*-caffeoyl)-β-D-glucopyranoside, which was named spiraearhamnin B.

Acylated rhamnetin glycosides still represent a rare flavonoid group with only two known members, i.e., 3″-*O*-*p*-coumaroylxanthorhamnin B [rhamnetin-3-*O*-(3‴-*O*-*p*-coumaroyl)rhamnoside] from *Rhamnus petiolaris* Boiss. (Rhamnaceae) [12] and campylospermoside F [rhamnetin-4′-*O*-(6″-*O*-*p*-coumaroyl)-β-D-glucopyranoside] from *Ouratea calantha* Gilg [*Campylospermum calanthum* (Gilg) Farron, Ochnaceae] [17].

The occurrence of rhamnetin (**1**) in the genus *Spiraea* was determined using chromatography of acid-hydrolyzed alcohol extracts from seven *Spiraea* species. Two species that were representatives of the subgenus *Protospiraea* like *S. salicifolia*, i.e., *S. betulifolia* and *S. betulifolia* var. *aemiliana*, contained **1** in addition to kaempferol, quercetin, and isorhamnetin. The main flavonoid aglycons from species of the subgenus *Metaspiraea*, i.e., *S. alpina*, *S. chamaedryfolia*, *S. dahurica*, *S. hypericifolia*, and *S. media*, were quercetin, kaempferol, and isorhamnetin. Compound **1** was not observed in these species. Chromatography of the EtOAc fraction of *S. betulifolia* detected **2** and flavonol glycosides that were identified as astragalin (**5**), nicotiflorin (**6**), tiliroside (**7**), isoquercitrin (**8**), hyperoside (**9**), avicularin (**10**), rutin (**11**), helichrysoside (**12**), quercetin-3-*O*-(6″-caffeoyl)-β-D-glucopyranoside (**13**), and isorhamnetin-3-*O*-β-D-glucopyranoside (**14**). Runners of *S. betulifolia* var. *aemiliana* yielded **2**, **7**–**9**, **11**, **12**, and **14**. The chemistry of *S. betulifolia* and *S. betulifolia* var. *aemiliana* was studied for the first time.

Thus, the results showed that the genus *Spiraea* contained kaempferol, quercetin, and isorhamnetin and possibly also rhamnetin, the distribution of which was probably limited to species of the subgenus *Protospiraea*.

TABLE 1. PMR (500 MHz) and $^{13}C$ NMR Spectra (125 MHz) of **3** and **4** (MeOH-$d_4$, δ, ppm, J/Hz)

| C atom | **3** | | **4** | |
|---|---|---|---|---|
| | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ |
| | | Rhamnetin | | |
| 2 | – | 157.2 | – | 156.9 |
| 3 | – | 133.5 | – | 133.2 |
| 4 | – | 177.0 | – | 177.2 |
| 5 | – | 161.0 | – | 160.9 |
| 6 | 6.35 (1H, d, J = 2.1) | 97.3 | 6.40 (1H, d, J = 2.0) | 97.5 |
| 7 | – | 164.8 | – | 165.0 |
| 8 | 6.65 (1H, d, J = 2.2) | 92.5 | 6.62 (1H, d, J = 2.1) | 92.0 |
| 9 | – | 156.3 | – | 156.4 |
| 10 | – | 103.9 | – | 104.2 |
| 1′ | – | 122.6 | – | 122.7 |
| 2′ | 7.72 (1H, d, J = 2.0) | 116.0 | 7.75 (1H, d, J = 2.1) | 115.9 |
| 3′ | – | 145.0 | – | 144.8 |
| 4′ | – | 148.6 | – | 148.5 |
| 5′ | 6.93 (1H, d, J = 9.0) | 115.5 | 6.94 (1H, d, J = 9.1) | 115.3 |
| 6′ | 7.66 (1H, dd, J = 9.0, 2.0) | 120.4 | 7.69 (1H, dd, J = 9.1, 2.1) | 121.0 |
| 7-$OCH_3$ | 3.85 (3H, s) | 56.2 | 3.81 (3H, s) | 56.2 |
| | | 3-*O*-β-D-Glucopyranosyl | | |
| 1″ | 5.44 (1H, d, J = 7.1) | 100.5 | 5.37 (1H, d, J = 7.0) | 100.3 |
| 2″ | | 73.7 | | 73.9 |
| 3″ | 3.07–3.35 (4H, m) | 76.9 | 3.04–3.31 (4H, m) | 76.5 |
| 4″ | | 70.1 | | 70.0 |
| 5″ | | 77.5 | | 77.7 |
| 6″ | 4.45 (1H, dd, J = 11.5, 2.3) | 64.1 | 4.40 (1H, dd, J = 11.6, 2.3) | 63.8 |
| | 4.63 (1H, dd, J = 11.5, 5.3) | | 4.69 (1H, dd, J = 11.6, 5.4) | |
| | 6″-*O*-*p*-Coumaroyl | | 6″-*O*-Caffeoyl | |
| 1‴ | – | 126.4 | | 127.0 |
| 2‴ | 7.92 (2H, d, J = 9.0) | 129.8 | 7.12 (1H, d, J = 2.0) | 115.0 |
| 3‴ | 6.78 (2H, d, J = 9.0) | 116.8 | – | 146.5 |
| 4‴ | – | 157.9 | – | 148.0 |
| 5‴ | 6.78 (2H, d, J = 9.0) | 116.8 | 6.80 (1H, d, J = 8.0) | 116.5 |
| 6‴ | 7.92 (2H, d, J = 9.0) | 129.8 | 6.89 (1H, dd, J = 8.0, 2.1) | 123.3 |
| 7‴ | 7.40 (1H, d, J = 16.0) | 145.6 | 7.45 (1H, d, J = 16.0) | 145.6 |
| 8‴ | 6.28 (1H, d, J = 16.0) | 114.3 | 6.12 (1H, d, J = 16.0) | 114.5 |
| 9‴ | – | 166.5 | – | 166.2 |

## EXPERIMENTAL

**General Comments.** Column chromatography (CC) used $SiO_2$, reversed-phase $SiO_2$ (RP-$SiO_2$), polyamide (Sigma-Aldrich, St. Louis, MO, USA), and Sephadex LH-20 (GE Healthcare, Little Chalfont, UK). IR spectra were recorded from KBr pellets (1:100) on an FT-801 FTIR spectrometer (NPF Simex, Novosibirsk, Russia). Spectrophotometric studies used an SF-2000 spectrophotometer (OKB Spektr, St. Petersburg, Russia); mass spectrometric, an LCMS-8050 TQ-mass spectrometer (Shimadzu, Columbia, MD, USA) with electrospray ionization (ESI, positive-ion mode), ESI interface temperature 300°C, desolvation line temperature 250°C, heating block temperature 400°C, spraying gas ($N_2$) flow rate 3 L/min, heating gas (air) flow rate 10 L/min, collision-induced dissociation gas (CID gas, Ar) pressure 270 kPa, Ar flow rate 0.3 mL/min, capillary potential 3 kV, and mass scan range (*m*/*z*) 100–1,000. NMR spectra were recorded on a VXR 500S NMR spectrometer (Varian, Palo Alto, CA, USA). Preparative HPLC used a Summit liquid chromatograph (Dionex, Sunnyvale, CA, USA).

**Plant Material.** Runners of *Spiraea* species were collected during flowering in various districts of Russia: *S. alpina* Pall., in the vicinity of Nilov Desert (Tunkinskii District, Republic of Buryatia; Jul. 21, 2016; 51°51′15″ N, 101°43′3″ E,

h 2,318 m above sea level); *S. betulifolia* Pall., Nizhnetambovskoe village (Komsomol′skii District, Khabarovskii Krai, Jul. 14, 2014; 50°57′31″ N, 159°56′15″ E, h 84 m above sea level); *S. betulifolia* var. *aemiliana* (C. K. Schneid.) Koidz. (syn. *S. beauverdiana* C. K. Schneid.), Kozyrevsk town (Ust-Kamchatskii District, Kamchatskii Krai; Jul. 21, 2016; 56°1′40″ N, 138°8′26″ E, h 96 m above sea level); *S. chamaedryfolia* L. (syn. *S. flexuosa* Fisch. ex Cambess., *S. ussuriensis* Pojark.), Boyarsk village (Kabanskii District, Republic of Buryatia; Jun. 12, 2015; 51°50′57″ N, 106°4′12″ E, h 458 m above sea level); *S. dahurica* (Rupr.) Maxim., Malovskii town (Bauntovskii District, Republic of Buryatia; Jul. 20, 2014; 54°23′34″ N, 113°33′15″ E, h 867 m above sea level); *S. hypericifolia* L. (syn. *S. aquilegiifolia* Pall.), in the vicinity of Merkit Fortress (Mukhorshibirskii District, Republic of Buryatia; Jun. 19, 2016; 51°9′6″ N, 107°6′30″ E, h 928 m above sea level); *S. media* Schmidt (syn. *S. sericea* Turcz.), in the vicinity of Sukhoi Ruchei (Kabanskii District, Republic of Buryatia; Jun. 18, 2015; 51°48′33″ N, 106°1′22″ E, h 435 m above sea level); and *S. salicifolia* L., Kyren village (Tunkinskii District, Republic of Buryatia; Jul. 20, 2015; 51°40′48″ N, 102°11′54″ E, h 741 m above sea level). The species were determined by Dr. T. A. Aseeva (IGEB, SB, RAS). Raw material was dried in a convection oven (50°C) to ≤5% moisture content.

**Isolation of 1–4 from *S. salicifolia*.** The extraction conditions and production of the EtOAc fraction (SF-2) and its subfractions (SF-2/3-01, SF-2/3-06) were reported earlier [9]. Subfraction SF-2/3-01 was separated over $SiO_2$ (CC, 1 × 30 cm) using a hexane–EtOAc gradient (95:5) to isolate rhamnetin (**1**, 18 mg) [18]. Subfraction SF-2/3-06 was chromatographed over $SiO_2$ (CC, 3 × 30 cm; hexane–EtOAc, 92:8) and then by preparative HPLC [LiChrospher PR-18 column (250 × 10 mm, ∅ 10 μm,; Supelco, Bellefonte, PA, USA); mobile phase $H_2O$ (A) and MeCN (B); gradient mode (%B): 0–40 min, 40–60%; 40–60 min, 60–90%; flow rate ν 1 mL/min; column temperature 30°C, UV detector at 350 nm] to afford rhamnetin-3-*O*-*β*-D-glucopyranoside (**2**, 26 mg) [14], **3** (37 mg), and **4** (28 mg).

**Spiraearhamnin A (3).** $C_{31}H_{28}O_{14}$. HR-ESI-MS *m*/*z* 625.218 $[M + H]^+$; calcd 625.591. (+)ESI-MC *m*/*z*: 625 $[M + H]^+$, 479 $[(M + H) – 146]^+$, 317 $[(M + H) – 146 – 162]^+$. UV spectrum (MeOH, $\lambda_{max}$, nm): 258, 317, 361. IR spectrum ($\nu_{max}$, $cm^{-1}$): 3341, 1720, 1641, 1625, 1604. Table 1 presents the PMR (500 MHz) and $^{13}C$ NMR spectra (125 MHz).

**Spiraearhamnin B (4).** $C_{31}H_{28}O_{15}$. HR-ESI-MS *m*/*z* 641.402 ($[M + H]^+$; calcd 641.591. (+)ESI-MC *m*/*z*: 641 $[M + H]^+$, 479 $[(M + H) – 162]^+$, 317 $[(M + H) – 2 × 162]^+$. UV spectrum (MeOH, $\lambda_{max}$, nm): 256, 334, 368. IR spectrum ($\nu_{max}$, $cm^{-1}$): 3327, 1725, 1637, 1620, 1601. Table 1 presents the PMR (500 MHz) and $^{13}C$ NMR spectra (125 MHz).

**Acid Hydrolysis of 3 and 4.** The compound (5 mg) was dissolved in TFA (10 mL, 5%) and heated at 110°C for 2 h. The hydrolysate was concentrated *in vacuo*, dissolved in MeOH, and chromatographed over polyamide (CC, 20 g) with elution successively by $H_2O$ (100 mL, eluate I) and EtOH (90%, 250 mL, eluate II). The obtained eluates were concentrated *in vacuo* and analyzed by HPLC (conditions 1, monosaccharides as 3-methyl-1-phenyl-2-pyrazolin-5-one derivatives [19]; conditions 2, phenolic compounds). Eluate I was also analyzed as before to determine if the monosaccharides were the D- or L-form [20]. Eluate I after hydrolysis of **3** and **4** contained glucose ($t_R$ 12.50 min); eluate II, rhamnetin ($t_R$ 14.51 min); in addition to *p*-coumaric acid for **3** ($t_R$ 8.12 min) and caffeic acid for **4** ($t_R$ 6.89 min). Eluates II were also separated over $SiO_2$ (CC, 1 × 15 cm, hexane–EtOAc, 100:0→60:40) to isolate from **3** rhamnetin (**3a**, 2 mg) and *p*-coumaric acid (1 mg) [11] and from **4**, rhamnetin (**3a**, 2 mg) [18] and caffeic acid (1 mg) [21].

**Rhamnetin (3a).** $C_{16}H_{12}O_7$. (+)ESI-MC *m*/*z*: 317 $[M + H]^+$, 302 $[(M + H) – 15]^+$. UV spectrum (MeOH, $\lambda_{max}$, nm): 257, 369. $^{13}C$ NMR spectrum (125 MHz, MeOH-$d_4$, δ, ppm): 146.8 (C-2), 136.3 (C-3), 176.0 (C-4), 160.3 (C-5), 97.3 (C-6), 164.9 (C-7), 92.0 (C-8), 156.1 (C-9), 104.3 (C-10), 122.5 (C-1′), 115.8 (C-2′), 145.0 (C-3′), 148.4 (C-4′), 115.4 (C-5′), 120.3 (C-6′), 56.1 (7-O<u>C</u>$H_3$).

**Acid Hydrolysis of *Spiraea* Extracts.** A weighed portion of plant raw material (0.4 g) was mixed with hexamethylenetetramine solution (1 mL, 0.5%), $Me_2CO$ (20 mL), and HCl solution (7 mL, 25%), refluxed for 30 min, and cooled. The extract was filtered, treated with $H_2O$ (25 mL) and EtOAc (25 mL), and shaken for 5 min. The organic layer was separated, washed with $H_2O$ (2 × 50 mL), filtered through anhydrous $Na_2SO_4$, concentrated, and analyzed by HPLC (conditions 2).

**HPLC.** Conditions 1: ProntoSIL-120-5-C18 AQ column (2 × 75 mm, ∅ 5 μm; Metrohm AG); mobile phase $CH_3COONH_4$ (100 mM, pH 4.5) (A) and MeCN (B); gradient mode (%B): 0–20 min, 20–26%; flow rate 150 μL/min; column temperature 35°C, UV detector at 250 nm. The retention times of standard samples ($t_R$, min) were mannose 6.83, glucose 12.52, and galactose 13.54. Conditions 2: ProntoSIL-120-5-C18 AQ column (2 × 75 m, ∅ 5 μm; Metrohm AG); mobile phase $LiClO_4$ (0.2 M) in $HClO_4$ (0.006 M) (A) and MeCN (B); gradient mode (%B): 0–9 min, 0–80%; 9–15 min, 80–100%; flow rate 100 μL/min; column temperature 35°C; UV detector at 320 and 350 nm. The retention times of standard samples ($t_R$, min) were caffeic acid 6.90, *p*-coumaric acid 8.10, *o*-coumaric acid 9.73, quercetin 11.48, kaempferol 13.07, isorhamnetin 13.45, tamarixetin 13.84, and rhamnetin 14.52.

Chromatographic separation of phenolic compounds from runners of *S. betulifolia* and *S. betulifolia* var. *aemiliana* used CC over $SiO_2$, RP-$SiO_2$, polyamide, and Sephadex LH-20 and preparative HPLC as described earlier [9] to isolate from *S. betulifolia* (630 g) 11 compounds that were identified using UV, IR, and NMR spectroscopy and mass spectrometry as **2** (8 mg), astragalin (**5**, 12 mg) [22], nicotiflorin (**6**, 10 mg) [23], tiliroside (**7**, 63 mg) [24], isoquercitrin (**8**, 12 mg) [25], hyperoside (**9**, 34 mg) [22], avicularin (**10**, 12 mg) [22], rutin (**11**, 39 mg) [25], helichrysoside (**12**, 46 mg) [26], quercetin-3-*O*-(6″-caffeoyl)-*β*-D-glucopyranoside (**13**, 40 mg) [3], and isorhamnetin-3-*O*-*β*-D-glucopyranoside (**14**, 9 mg) [27]. Chromatographic separation of *S. betulifolia* var. *aemiliana* (320 g) isolated 7 compounds that included **2** (6 mg), **7** (21 mg), **8** (5 mg), **9** (11 mg), **11** (18 mg), **12** (14 mg), and **14** (2 mg).


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