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BIOLOGICALLY ACTIVE COMPOUNDS FROM *Limonium Gmelinii* AND *L. Popovii*. I

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Compositions of ethylacetate fractions of roots and aerial parts of Limonium Gmelinii *and* L. Popovii *(Plumbaginaceae) were studied. 3,5,7,3′,4′,6′-Hexahydroxyflavone and myricetin 3-O-α-L-(2′-galloyl)arabopyranoside, the structures of which were established using chemical transformations and spectral data, were isolated for the first time.*

Key words: *Limonium Gmelinii*, *L. Popovii*, Plumbaginaceae, flavonoids, 3,5,7,3′,4′,6′-hexahydroxyflavone, myricetin 3-O-α-L-(2′-galloyl)arabinopyranoside

Concentrated methanolic extracts of roots and aerial parts of *Limonium Gmelinii* and *L. Popovii* were successively fractionated with petroleum ether, chloroform, diethylether, ethylacetate, and butanol.

The ethylacetate fractions were chromatographed over polyamide columns with elution by $CHCl_3$ and $CHCl_3$:CH_3OH mixtures (9:1, 1:1, and 1:9). Identical fractions were combined and rechromatographed over polyamide, silica gel, and Sephadex LH-20.

Roots of Gmelin sea-lavender afforded D-(+)-galactose (**1**) [1]; gallic (**2**) [2], syringic (**3**) [3], and ellagic (**4**) [4] acids; quercetin (**5**) [5, 6]; rutin (**6**) [7]; myricetin (**7**) [8] and its glycosides: myricetrin (**8**) [9, 10], 7-O-α-L-rhamnopyranoside (**9**) [11], rutinoside (**10**) [7], 3-O-α-L-arabopyranoside (**11**) [12], 3-O-β-D-xyloside (**12**) [13], 3-O-α-L-(2″-O-α-rhamnopyranosyl)rhamnopyranoside (**13**) [14], and (-)-epigallocatechin-3-O-gallate (**14**) [15] in addition to the new, previously undescribed 3,5,7,3′,4′,6′-hexahydroxyflavone (**15**) and myricetin 3-O-α-L-(2′-galloyl)arabopyranoside (**16**).

We identified **2**, **5**, **7**, **8**, **14**, **15**, **16**, and myricetin 3-O-β-D-(6″-galloyl)galactopyranoside (**17**) [12] in the aerial part of Gmelin sea-lavender.

Roots of Popov sea-lavender afforded **2**, **5**, and **7**; the aerial part, **2**, **5**, **7**, **8**, **17**, and myricetin 3-O-β-D-galactopyranoside (**18**) [9, 16], 3-O-β-D-glucopyranoside (**19**) [17], and 3-O-β-D-(6″-galloyl)glucopyranoside (**20**) [18].

All compounds were identified by IR, mass, PMR, and ^{13}C NMR spectra; chemical transformations, and comparison with the literature.

3,5,7,3′,4′,6′-Hexahydroxyflavone is a new and previously undescribed compound, yellowish-green, mp 306-308°C. Qualitative reactions and chromatographic behavior [paper (PC) and thin-layer (TLC)] indicated that it is a flavone with a free 3-OH group [19].

Two doublets in the PMR with spin—spin coupling constants (SSCC) 2 Hz near 6.21 and 6.45 ppm are consistent with *meta*-substitution of ring A [21]. A doublet with SSCC 1.8 Hz near 7.69 ppm and a broad singlet near 7.8 ppm may belong to H-2′ and H-5′ or H-3′ and H-6′ of ring B.

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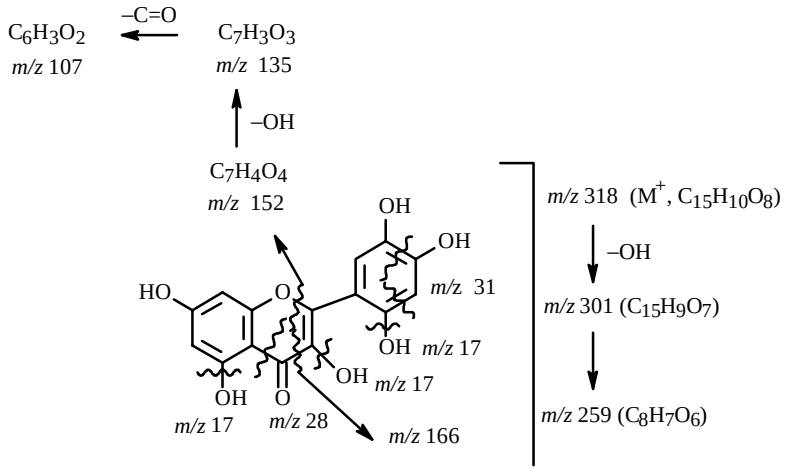


Scheme 1. Proposed fragmentation scheme of 3,5,7,3′,4′,6′-hexahydroxyflavone.

The ^{13}C NMR spectrum contains signals for 15 C atoms. The positions of signals for ring A agree completely with the literature for a 5,7-dihydroxysubstituted flavonol with a free 3-OH. C-6 is near 98.25 ppm; C-8, 93.347 ppm [22]. A doublet for C-2′ appears near 111.52 ppm; C-5′, 114.09 also as a doublet. *Ortho*-substituted C-3′ and C-4′ resonate near 141.18 and 140.11 ppm; C-6′, 146.13 ppm.

Bathochromic shifts of bands induced by $AlCl_3$ in the UV spectrum are retained upon addition of HCl and indicate free C-3 and C-5 hydroxyls. Bathochromic shifts of the second band with NaOAc and of the first with H_3BO_3 are indicative of a free 7-OH in ring A and an *ortho*-dihydroxy in ring B.

The molecular weight (EI method) of 318 corresponds with the empirical formula $C_{15}H_{10}O_8$. A characteristic fragment with *m*/*z* 152 arises from retro-decomposition according to the proposed fragmentation scheme (Scheme 1) [20].

Myricetin 3-O-α-L-(2′-galloyl)arabinopyranoside, $[M]^+$ 603, $C_{27}H_{23}O_{16}$, is also new and not previously described. It is a yellow compound, mp 182-184°C. Qualitative reactions and chromatographic behavior (PC and TLC) indicated that it is a flavonol glycoside with a substituted 3-OH [19].

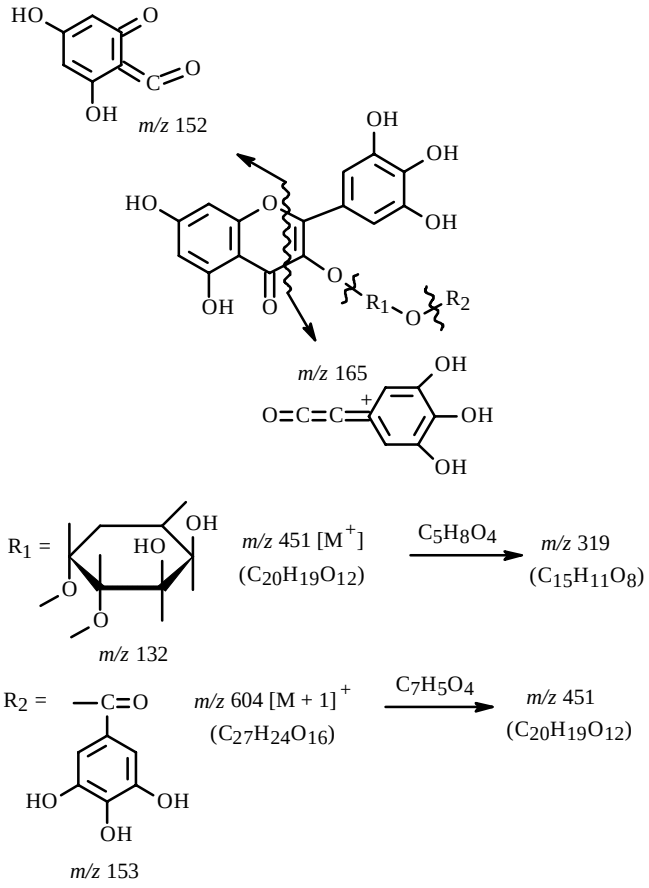
Stepwise hydrolysis with time and PC after 20 min detected gallic acid and an intermediate glycoside; after 60 min, the aglycon, gallic acid, and arabinose. The chromatographic behavior, PMR spectrum, and lack of melting-point depression in a mixed sample identified the aglycon as myricetin. PC using systems 2 and 4 detected gallic acid and arabinose in the hydrolysis products.

Absorption bands in the IR spectrum near 3300-3400 cm^{-1} (OH), 1654-1670 (C=O), and three strong bands at 1028, 1070, and 1086 indicate the pyranose form of the sugar. A band near 836 cm^{-1} corresponds with the α-glycoside bond.

The mass spectrum (positive-ion FAB) gave a peak for the molecular ion with *m*/*z* 604, corresponding with $C_{27}H_{24}O_{16}$, and a peak for an ion with *m*/*z* 318 (EI), $C_{15}H_{10}O_8$. The presence of gallic acid in the structure was confirmed by formation of a fragment with *m*/*z* 450, corresponding to loss of acid, and a fragment with *m*/*z* 318, corresponding to loss of arabinose. A characteristic fragment with *m*/*z* 152 corresponds to retro-decomposition of flavonoids [20]. The proposed fragmentation scheme of myricetin 3-O-α-L-(2′-galloyl)arabinopyranoside is given below.

A 2H-singlet near 7.08 ppm corresponds to gallic-acid protons; a 1H-doublet near 5.17 with SSCC 6.6 Hz, to H′ of α-L-arabinose. The attachment site of gallic acid and the sugar was determined as C-3 using ^{13}C NMR spectra and HMBC two-dimensional spectra.

The ^{13}C NMR spectrum exhibits 27 C atoms. The positions of signals for rings A and B correspond with literature data for myricetin, arabinose, and gallic acid [22].



Scheme 2. Proposed fragmentation scheme of myricetin 3-O-α-L-(2′-galloyl)arabinopyranoside.

EXPERIMENTAL

We used PC and TLC and solvent systems: $CHCl_3$:CH_3OH (95:5, 90:10, 85:15) (1), *n*-butanol:CH_3CO_2H:H_2O (40:12, 5:29) (2), CH_3CO_2H (2%) (3), and *n*-butanol:C_5H_5N:H_2O (6:4:3) (4).

TLC was performed on Silicagel 60 F 254 (Merck) plates with identification in UV light and reaction with cerium sulfate at 100-105°C in system 1; PC, on Filtrak No. 3 chromatography paper with identification in UV light and reaction with ammonia vapor, $AlCl_3$, and ferric-ammonium alum in systems 2 and 3. Carbohydrates were detected using *o*-toluidine with heating for 3-5 min at 90-100°C in system 4.

Extraction and Isolation of Phenolic Acids and Flavonoids. Air-dried raw material was ground to 1-3 mm and extracted three times with CH_3OH at room temperature (1:4 material:solvent ratio). The methanol extract was evaporated to a small volume and fractionated successively with petroleum ether, $CHCl_3$, diethylether, ethylacetate, and butanol.

The ethylacetate extracts were chromatographed over polyamide columns, silica gel (Silicagel 60, 70-230 mesh, Merck), and Sephadex (LH-20) with elution by $CHCl_3$, $CHCl_3$:CH_3OH mixtures (19:1, 9:1, 4:1, and 1:1), and CH_3OH. Elution from Sephadex columns used H_2O:CH_3OH mixtures (95:5, 9:1, 5:1, and 1:1) and CH_3OH. Pure compounds were isolated by rechromatography using the identical columns and eluents.

Acid hydrolysis was performed in HCl (2 N) for 2 h on a boiling-water bath. The aglycon was extracted by ethylacetate. Sugar was identified by PC using system 3.

Stepwise hydrolysis with time was performed in HCl (0.2 N) in ethanol for 2 h on a boiling-water bath. The hydrolysis products were identified by PC using system 2.

IR spectra were recorded on JASCO IR A-1 and Shimadzu IR-460 instruments; UV spectra, on a Shimadzu UV-240; PMR spectra, on Bruker AM 200, 300, 400, and 500 FT NMR instruments; ^{13}C NMR spectra, on a Bruker AM 500 FT NMR

at 50 and 125 MHz; mass spectra, on Varian-MAT 112S and Finnigan MAT 112 instruments; EI mass spectra, on a JEOL MAT 312 JMS HX-100 instrument. Optical rotations were determined on a JASCO DIP-360 instrument.

D-(+)-Galactose, $[M]^+$ 180, mp 158-160°C, $[\alpha]_D^{27}$ 83.6° (*c* 0.11, MeOH).

EI mass spectrum: 180 $[M]^+$, 149 (2), 131 (3), 103 (13), 85 (11), 73 (100), 61 (68), 57 (48).

PMR spectrum (DMSO, 400 MHz, δ, ppm, J/Hz): 3.02 (1H, m), 3.09 (1H, m), 3.41 (2H, m), 3.53 (2H, m), 4.33 (1H, t, J = 5.7), 4.43 (1H, d, J = 6.5), 4.62 (1H, d, J = 4.2), 4.87 (1H, d, J = 5), 4.89 (1H, t, J = 3.7), 6.16 (1H, d, J = 4.2).

^{13}C NMR spectrum (CD_3OD, 50 MHz): 61.275 (C-6), 70.657 (C-4), 71.955 (C-2), 72.411 (C-3), 73.151 (C-5), 92.264 (C-1).

Gallic acid, $[M]^+$ 170, mp 221-223°C.

UV spectrum (MeOH, λ_{max}, nm): 270.

EI mass spectrum: 170 $[M]^+$, 153 (86), 135 (11), 125 (23), 107 (8), 79 (25), 56 (11), 54 (30), 52 (50).

PMR spectrum (CD_3OD, 500 MHz, δ, ppm): 7.04 (2H, s, H-6 and H-8).

Syringic acid, $[M]^+$ 198, mp 208-210°C.

UV spectrum (MeOH, λ_{max}, nm): 275.

PMR spectrum (CD_3OD, 500 MHz, δ, ppm): 7.01 (2H, s, H-6 and H-8), 3.82 (6H, s, OCH_3-3,5).

Ellagic acid, $C_{14}H_6O_8$, $[M]^+$ 270, mp 360°C.

UV spectrum (MeOH, λ_{max}, nm): 257, 360.

The compound gives a red color with CH_3CO_2H (conc.) and $NaNO_2$, characteristic of free ellagic acid. The melting point of a mixed sample with ellagic acid was not depressed.

Quercetin, $[M]^+$ 302, mp 310-312°C.

UV spectrum (MeOH, λ_{max}, nm): 256, 340 sh, 372.

PMR spectrum (CD_3OD, 200 MHz, δ, ppm, J/Hz): 6.17 (1H, d, J = 1.7, H-6), 6.38 (1H, d, J = 1.5, H-8), 6.86 (1H, d, J = 8.5, H-5′), 7.62 (1H, d, J = 8, H-2′), 7.7 (1H, d, J = 8, H-6′).

Rutin (quercetin-3-O-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside], $[M]^+$ 609, mp 198-200°C.

UV spectrum (MeOH, λ_{max}, nm): 262, 304, 374.

PMR spectrum (CD_3OD, 400 MHz, δ, ppm, J/Hz): 0.84 (3H, d, J = 6, CH_3-rhamn.), 3.29-3.80 (sugar region), 4.2 (1H, s, H-1″), 5.7 (1H, d, J = 7.5, H-1‴), 6.08 (1H, d, J = 2), 6.36 (1H, d, J = 2), 6.78 (1H, d, J = 9, H-5′), 7.62 (1H, d, J = 2, H-2′), 7.7 (1H, d, J = 2, H-6′). Acid hydrolysis produced myricetin, glucose, and rhamnose.

Myricetin, $[M]^+$ 318, mp 364-366°C.

UV spectrum (MeOH, λ_{max}, nm): 252, 340 sh, 374. IR spectrum (KBr, λ_{max}, cm^{-1}): 3385-3300, 1660, 1565, 1516.

PMR spectrum (CD_3OD, 500 MHz, δ, ppm, J/Hz): 6.17 (1H, d, J = 2), 6.37 (1H, d, J = 2), 7.34 (2H, s).

Myricetrin (myricetin 3-O-α-L-rhamnopyranoside), $[M]^+$ 364, mp 194-197°C, $[\alpha]_D^{27}$ -122.6° (*c* 0.06, MeOH).

UV spectrum (MeOH, λ_{max}, nm): 257, 352.

PMR spectrum (CD_3OD, 400 MHz, δ, ppm, J/Hz): 0.95 (3H, d, J = 6, CH_3-rhamn.), 3.25 (1H, t, H-5″), 3.62 (1H, dd, H-3″), 3.72 (1H, dd, H-2″), 4.98 (1H, dd, H-4″), 5.3 (1H, s, H-1″), 6.19 (1H, d, J = 2), 6.36 (1H, d, J = 2), 6.93 (2H, s).

^{13}C NMR spectrum (DMSO, 125 MHz): 17.59 (CH_3-rhamn.), 70.718 (C-5″), 70.509 (C-2″), 70.647 (C-3″), 71.401 (C-4″), 93.692 (C-8), 98.844 (C-6), 102.019 (C-1″), 104.093 (C-10), 108.052 (C-2′,6′), 119.73 (C-1′), 134.39 (C-3), 136.618 (C-4′), 145.859 (C-3′,5′), 156.553 (C-9), 157.562 (C-2), 161.397 (C-5), 164.47 (C-7), 177.845 (C-4). Acid hydrolysis produced myricetin and rhamnose.

Myricetin 7-O-α-L-rhamnopyranoside, $[M]^+$ 464, mp 178-180°C, $[\alpha]_D^{27}$ -135.3° (*c* 0.06, MeOH).

UV spectrum (MeOH, λ_{max}, nm): 262, 304 sh, 355; +NaOAc: 256, 389.

PMR spectrum (CD_3OD, 400 MHz, δ, ppm, J/Hz): 1.00 (3H, d, J = 6, CH_3), 3.29 (1H, m, H-5″), 3.54 (1H, m, H-3″), 3.88 (1H, dd, H-2″), 4.25 (1H, s, H-4″), 5.36 (1H, s, H-1″), 6.23 (1H, d, J = 2), 6.39 (1H, d, J = 2), 6.99 (2H, s). Acid hydrolysis produced myricetin and rhamnose.

Myricetin rutinoside (myricetin 3-O-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside], $[M]^+$ 626, mp 190-192°C.

UV spectrum (MeOH, λ_{max}, nm): 256, 308, 363.

PMR spectrum (CD_3OD, 400 MHz, δ, ppm, J/Hz): 0.96 (3H, d, J = 6, CH_3-rhamn.), 3.12-4.56 (sugar region), 4.56 (1H, s, H-1″), 5.31 (1H, d, J = 6.5, H-1‴), 6.19 (1H, d, J = 2), 6.35 (1H, d, J = 2), 6.94 (2H, s). Acid hydrolysis produced myricetin, glucose, and rhamnose.

Myricetin 3-O-α-L-arabinopyranoside, $[M]^+$ 450, mp 203-205°C, $[\alpha]_D^{27}$ -112° (*c* 0.012, MeOH).

UV spectrum (MeOH, λ_{max}, nm): 257, 363.

PMR spectrum (CD_3OD, 500 MHz, δ, ppm, J/Hz): 3.45 (1H, d, J = 11.6, H-4″), 3.63 (1H, dd, J = 3, H-5″), 3.82-3.90 (2H, m, H-2″ and H-3″), 5.17 (1H, d, J = 6.7, H-1″), 6.19 (1H, d, J = 2, H-6), 6.35 (1H, d, J = 2, H-8), 7.3 (2H, s, H-2′ and H-6′). Acid hydrolysis produced myricetin and arabinose.

Myricetin 3-O-β-D-xylopyranoside, $[M]^+$ 450, mp 185-187°C, $[\alpha]_D^{27}$ -28° (*c* 0.04, MeOH).

UV spectrum (MeOH, λ_{max}, nm): 256, 284 sh, 360.

PMR spectrum (CD_3OD, 200 MHz, δ, ppm, J/Hz): 3.51 (1H, dd, J = 3, H-5″), 3.68 (1H, dd, J = 3, H-4″), 3.82-3.90 (2H, m, H-2″ and H-3″), 5.21 (1H, d, J = 5.8, H-1″), 6.23 (1H, d, J = 2), 6.42 (1H, d, J = 2), 7.34 (2H, s). Acid hydrolysis produced myricetin and xylose.

Myricetin 3-O-α-L-(2″-O-α-rhamnopyranosyl)rhamnopyranoside, $[M]^+$ 611, mp 183-185°C.

UV spectrum (MeOH, λ_{max}, nm): 258, 302 sh, 354; +$AlCl_3$: 272, 309, 424; +$AlCl_3$/HCl: 273, 307, 404; +NaOAc: 262, 299, 374.

PMR spectrum (CD_3OD, 400 MHz, δ, ppm, J/Hz): 0.97 (3H, d, J = 6, H-6‴), 1.27 (3H, d, J = 6, H-6″), 3.15 (1H, m, H-4‴), 3.32 (1H, m, H-4″), 3.50-3.57 (2H, m, H-5‴, H-5″), 3.75-3.79 (2H, m, H-3‴, H-3″), 4.20-4.24 (2H, t, H-2‴, H-2″), 4.55 (1H, br.s, H-1‴), 5.31 (1H, br.s, H-1″), 6.19 (1H, d, J = 1.8, H-6), 6.36 (1H, d, J = 1.8, H-8), 6.94 (2H, s, H-2′, H-6′). Acid hydrolysis produced myricetin and rhamnose.

Myricetin 3-O-β-D-(2′-galloyl)arabinopyranoside, $C_{27}H_{22}O_{16}$, $[M]^+$ 602, mp 182-184°C, $[\alpha]_D^{27}$ -36° (*c* 0.05, MeOH).

UV spectrum (MeOH, λ_{max}, nm): 265, 366; +$AlCl_3$: 272, 431; +$AlCl_3$/HCl: 269, 411; +NaOAc: 271, 388.

PMR spectrum (CD_3OD, 500 MHz, δ, ppm, J/Hz): 3.46 (1H, d, J = 9, H-4″), 3.63 (1H, dd, J = 2.5, H-5″), 3.82-3.91 (2H, m, H-2″, H-3″), 5.17 (1H, d, J = 6.6, H-1″), 6.19 (1H, d, J = 1.8, H-6), 6.38 (1H, d, J = 1.8, H-8), 7.08 (2H, s, gallic acid H-2‴, H-6‴), 7.32 (2H, s, H-2′, H-6′).

^{13}C NMR spectrum (DMSO, 50 MHz): 64.57 (C-5″), 66.313 (C-3″), 70.78 (C-4″), 71.896 (C-2″), 93.57 (C-8), 98.814 (C-6), 101.824 (C-1″), 103.99 (C-10), 108.59 (C-2′, C-6′), 108.876 (C-2‴, C-6‴), 119.97 (C-1′), 120.71 (C-1‴), 134.021 (C-3), 136.91 (C-4′), 138.07 (C-4‴), 145.64 (C-3‴, C-5‴), 145.483 (C-3‴, C-5′), 156.387 (C-2), 156.539 (C-9), 161.304 (C-5), 164.35 (C-7), 167.67 (C=O), 177.605 (C-4). Acid hydrolysis produced myricetin, gallic acid, and arabinose.

(-)-Epigallocatechin-3-O-gallate, $C_{22}H_{18}O_{11}$, $[M]^+$ 458, mp 140-142°C.

UV spectrum (MeOH, λ_{max}, nm): 274; +$AlCl_3$: 295; +NaOAc: 281.

IR spectrum (KBr, λ_{max}, cm^{-1}): 3419, 2526, 1692, 1615, 1534, 1448.

PMR spectrum (CD_3OD, 500 MHz, δ, ppm, J/Hz): 2.79-2.86 (1H, dd, J = 2.3, H-4α), 2.94-3.02 (1H, dd, J = 4.5, H-4β), 4.96 (1H, s, H-2), 5.52 (1H, s, H-3), 5.56 (1H, d, J = 1.5, H-6), 5.59 (1H, d, J = 1.5, H-8), 6.49 (2H, s, H-2′, H-6′), 6.94 (2H, s, H-2″, H-6″).

^{13}C NMR spectrum (DMSO, 125 MHz): 26.715 (C-4), 69.87 (C-3), 78.461 (C-2), 95.844 (C-8), 96.492 (C-6), 99.38 (C-10), 106.835 (C-2′, C-6′), 110.213 (C-2″, C-6″), 121.39 (C-1‴), 130.733 (C-1′), 133.65 (C-4″), 146.14 (C-3″, C-5″), 146.53 (C-3′, C-5′), 157.64 (C-5), 157.67 (C-7, C-9), 167.603 (C=O).

3,5,7,3′,4′,6′-Hexahydroxyflavone, $[M]^+$ 318, mp 306-308°C.

UV spectrum (MeOH, λ_{max}, nm): 256, 301 sh, 377; +$AlCl_3$: 271, 460; +$AlCl_3$/HCl: 266, 355 sh, 433; +NaOAc: 270, 390; +H_3BO_3: 261, 387.

IR spectrum (KBr, λ_{max}, cm^{-1}): 3385-3300, 1660, 1565, 1516.

Mass spectrum (EI, *m/z*): 318 (100) $[M]^+$, 301 (17), 269 (4), 244 (8), 152 (38), 135 (18), 107 (10), 64 (49).

PMR spectrum (CD_3OD, 400 MHz, δ, ppm, J/Hz): 6.16 (1H, d, J = 1.6, H-6), 6.41 (1H, d, J = 2, H-8), 7.66 (1H, d, J = 1.6, H-5′), 7.75 (1H, d, J = 1.6, H-2′).

^{13}C NMR spectrum (DMSO, 125 MHz): 93.35 (d, C-8), 98.25 (d, C-6), 102.98 (C-10), 111.54 (d, C-2′), 114.092 (d, C-5′), 121.06 (C-1′), 136.12 (C-3), 140.11 (C-4′), 141.18 (C-3′), 146.13 (C-6′), 146.55 (C-2), 156.113 (C-9), 160.69 (C-5), 164.02 (C-7), 175.86 (C-4).

6″-Galloylmyricetin 3-O-β-D-galactopyranoside, $C_{28}H_{24}O_{17}$, $[M]^+$ 632, mp 212-216°C, $[\alpha]_D^{27}$ 16° (*c* 0.07, MeOH).

UV spectrum (MeOH, λ_{max}, nm): 266, 366; +$AlCl_3$: 274, 435; +$AlCl_3$/HCl: 274, 412.

PMR spectrum (CD_3OD, 400 MHz, δ, ppm, J/H): 3.59 (1H, dd, J = 3.3, H-5″), 3.78-3.9 (3H, m, H-3″, H-6″a, H-2″), 4.23-4.31 (2H, m, H-6″b, H-4″), 5.16 (1H, d, J = 7.8, H-1″), 6.15 (1H, d, J = 1.8, H-6), 6.34 (1H, d, J = 1.8, H-8), 6.89 (2H, s, gallic acid H-2‴, H-6‴), 7.34 (2H, s, H-2′, H-6′).

^{13}C NMR spectrum (DMSO, 125 MHz): 62.107 (C-6″), 68.043 (C-2″), 71.181 (C-3″), 72.642 (C-4″), 73.113 (C-5″), 94.013 (C-8), 99.597 (C-6), 102.627 (C-1″), 103.018 (C-10), 108.67 (C-2′, C-6′), 108.778 (C-2‴, C-6‴), 118.851 (C-1′), 119.699 (C-1‴), 133.611 (C-3), 137.520 (C-4′), 139.245 (C-4‴), 145.714 (C-3′, C-5′), 145.803 (C-3‴, C-5‴), 156.13 (C-2), 156.558 (C-9), 161.14 (C-5), 165.707 (C-7), 166.91 (C=O), 176.99 (C-4). Acid hydrolysis produced myricetin, gallic acid, and galactose.

Myricetin 3-O-*β*-D-galactopyranoside, [M]+ 480, mp 196-198°C.

UV spectrum (MeOH, λ_{max}, nm): 256, 308, 362; +$AlCl_3$: 274, 310, 430.

PMR spectrum (CD_3OD, 300 MHz, δ, ppm, J/Hz): 3.59 (1H, dd, J = 3.3, H-5″), 3.78-3.9 (3H, m, H-3″, H-6″*α*, H-2″), 4.23-4.31 (2H, m, H-6″*β*, H-4″), 5.25 (1H, d, J = 7.9, H-1″), 6.17 (1H, d, J = 1.8, H-6), 6.42 (1H, d, J = 1.8, H-8), 7.23 (2H, s, H-2′, H-6′). Acid hydrolysis produced myricetin and galactose.

Myricetin 3-O-*β*-D-glucopyranoside, $[M]^+$ 480, mp 275-277°C.

UV spectrum (MeOH, λ_{max}, nm): 256, 308, 364; +$AlCl_3$: 272, 310, 430.

PMR spectrum (CD_3OD, 300 MHz, δ, ppm, J/Hz): 3.31-3.51 (3H, m), 3.58 (1H, dd), 3.64 (1H, dd), 5.27 (1H, d, J = 7.9, H-1″), 6.20 (1H, d, J = 1.8, H-6), 6.39 (1H, d, J = 1.8, H-8), 7.29 (2H, s, H-2′, H-6′). Acid hydrolysis produced myricetin and glucose.

6″-Galloylmyricetin 3-O-*β*-D-glucopyranoside, $C_{28}H_{24}O_{17}$, $[M]^+$ 632, $[\alpha]_D^{27}$ -51° (*c* 0.08, MeOH).

UV spectrum (MeOH, λ_{max}, nm): 266, 301, 362; +$AlCl_3$: 276, 440; +$AlCl_3$/HCl: 274, 412.

PMR spectrum (CD_3OD, 400 MHz, δ, ppm, J/Hz): 3.42 (2H, m), 3.55 (1H, t, J = 8), 4.25 (1H, dd, J = 1.5), 4.37 (1H, dd, J = 5.7), 5.16 (1H, d, J = 7.8, H-1″), 6.15 (1H, d, J = 1.8, H-6), 6.34 (1H, d, J = 1.8, H-8), 6.89 (2H, s, gallic acid H-2‴, H-6‴), 7.34 (2H, s, H-2′, H-6′).

^{13}C NMR spectrum (DMSO, 125 MHz): 63.798 (C-6″), 69.937 (C-4″), 74.008 (C-5″), 74.578 (C-2″), 76.521 (C-3″), 93.419 (C-8), 98.676 (C-6), 101.256 (C-1″), 103.901 (C-10), 108.593 (C-2′, C-6′), 108.697 (C-2‴, C-6‴), 119.393 (C-1′), 120.069 (C-1‴), 133.635 (C-3), 136.714 (C-4′), 138.393 (C-4‴), 145.371 (C-3′, C-5′, C-3‴, C-5‴), 156.050 (C-2), 156.216 (C-9), 161.186 (C-5), 164.060 (C-7), 165.777 (C=O), 177.263 (C-4). Acid hydrolysis produced myricetin, gallic acid, and glucose.

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