FLAVONOIDS OF *Lycopus lucidus*

A. Malik[1] and M. P. Yuldashev[2] UDC 547.972

Plants of the *Lycopus* L. (Lamiaceae) genus are rich sources of flavonoids, coumarins, terpenoids, and tanning agents. Many of them are used in folk and scientific medicine [1, 2].

The aerial part of *Lycopus lucidus* Turcz. ex Benth. (shiny lycopus) is used in folk medicine as a tonic, cardiotonic, and wound-healing and pain relieving agent [1].

Ground air-dried raw material (2.0 kg) collected during flowering (June 1999) on the northeast slope of the Tien Shan mountains (Xinjiang region, PRC) was extracted with ethanol (5×) at room temperature.

The combined alcohol extract was evaporated in vacuum. The condensed solution was diluted with water and successively treated with petroleum ether, ethylacetate, and butanol. The solvents were removed to afford petroleum-ether (19.0 g), ethylacetate (27.0 g), and butanol (42.0 g) fractions.

The ethylacetate fraction was chromatographed over a silica-gel column with gradient elution by $CHCl_3$—CH_3OH (98:2-85:15) to afford **1-5**. These compounds were identified using UV, mass, and PMR spectra, chemical transformations, and comparison with authentic samples.

Chrysoeriol (1) (5,7,4′-trihydroxy-3′-methoxyflavone), $C_{16}H_{12}O_6$ (M^+ 300), mp 336-337°C (dec.), UV spectrum (EtOH, λ_{max}, nm): 254, 270, 350.

PMR spectrum (300 MHz, DMSO-d_6 + CCl_4, δ, ppm, J/Hz): proton signals at 3.70 (3H, s, OCH_3), 6.15 (1H, d, J = 2.0, H-6), 6.40 (1H, d, J = 2.0, H-8), 6.70 (1H, s, H-3), 6.90 (1H, d, J = 8.0, H-5′), 7.47 (2H, dd, J = 2.0 and J = 8.0, H-2′, H-6′), 9.50 (1H, br.s, 4′-OH), 10.35 (1H, br.s, 7-OH), 12.80 (1H, s, 5-OH) [2-4].

Luteolin (2) (5,7,3′,4′-tetrahydroxyflavone), $C_{15}H_{10}O_6$, mp 329-331°C (dec.), UV spectrum (EtOH, λ_{max}, nm): 260, 273 sh, 355. The mass spectrum of **2** has peaks with *m*/*z* 286 $[M]^+$, 258, 229, 213, 153, 149, 137, 129, 107, 91, 81, 69.

PMR spectrum (300 MHz, DMSO-d_6 + CCl_4, δ, ppm, J/Hz): proton signals at 6.12 (1H, d, J = 2.0, H-6), 6.37 (1H, d, J = 2.0, H-8), 6.47 (1H, s, H-3), 6.85 (1H, d, J = 8.0, H-5′), 7.38 (2H, dd, J = 2.0 and 8.0, H-2′, H-6′), 9.20, 9.35 (1H, br.s, each, 3′-OH, 4′-OH), 10.35 (1H, br.s, 7-OH), 12.82 (1H, s, 5-OH) [2, 3, 5].

Quercetin (3) (3,5,7,3′,4′-pentahydroxyflavone), $C_{15}H_{10}O_7$, mp 312-314°C, UV spectrum (MeOH, λ_{max}, nm): 257, 268, 370. The IR spectrum of **3** contains absorption bands of hydroxyls (3320 cm^{-1}), carbonyl of γ-pyrone (1665 cm^{-1}), and aromatic C=C bonds (1618, 1575, 1520 cm^{-1}). The mass spectrum of **3** has peaks with *m*/*z* 302 $[M]^+$, 273, 262, 153, 141, 137, 128, 110, 95, 69, 57.

PMR spectrum (300 MHz, DMSO-d_6 + CCl_4, δ, ppm, J/Hz): proton signals at 6.12 (1H, d, J = 2.0, H-6), 6.35 (1H, d, J = 2.0, H-8), 6.85 (1H, d, J = 8.0, H-5′), 7.52 (1H, dd, J = 2.0 and J = 8.0, H-6′), 7.67 (1H, d, J = 2.0, H-2′), 8.75, 8.87, 9.08 (1H, br.s, each, 3-OH, 3′-OH, 4′-OH), 10.35 (1H, s, 7-OH), 12.32 (1H, s, 5-OH) [2, 3, 6].

Cinaroside (4) (luteolin-7-O-β-D-glucoside), $C_{21}H_{20}O_{11}$, mp 240-242°C. UV spectrum (EtOH, λ_{max}, nm): 256, 268, 350. The IR spectrum of **4** contains absorption bands of hydroxyls (3500-3200 cm^{-1}), carbonyl of γ-pyrone (1665 cm^{-1}), aromatic C=C bonds (1560, 1510 cm^{-1}), and C–O of glycosides (1095, 1030 cm^{-1}).

PMR spectrum (300 MHz, DMSO-d_6 + CCl_4, δ, ppm, J/Hz): proton signals at 3.10-3.90 (sugar protons), 5.02 (1H, d, J = 7.0, H-1″), 6.40 (1H, d, J = 2.0, H-6), 6.58 (1H, s, H-3), 6.75 (1H, d, J = 2.0, H-8), 6.85 (1H, d, J = 8.0, H-5′), 7.36 (2H, dd, J = 2.0 and J = 8.0, H-2′, H-6′), 12.87 (1H, br.s, 5-OH).

Acid hydrolysis of **4** produced luteolin and D-glucose.

Acetylation of **4** by acetic anhydride in pyridine isolated the hepta-acetyl derivative with mp 114-116°C, the mass spectrum of which contained the molecular ion with *m*/*z* 742 and strong peaks for fragments of the tetra-acetylhexose with *m*/*z*

1) Xinjiang University, Urumchi, PRC; 2) S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 83-84, January-February, 2002. Original article submitted February 4, 2002.

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331, 271, 229, and 169 [2, 3, 6].

Quercimeritrin (5) (quercetin-7-O-β-D-glucoside), $C_{21}H_{20}O_{12}$, mp 249-250°C. UV spectrum (EtOH, λ_{max}, nm): 258, 371; $+CH_3COONa$: 259, 371.

PMR spectrum (300 MHz, DMSO-d_6 + CCl_4, δ, ppm, J/Hz): proton signals at 3.05-3.90 (sugar protons), 5.00 (1H, d, J = 7.0, H-1″), 6.38 (1H, d, J = 2.0, H-6), 6.70 (1H, d, J = 2.0, H-8), 6.85 (1H, d, J = 8.0, H-5′), 7.55 (1H, dd, J = 2.0 and J = 8.0, H-6′), 7.70 (1H, d, J = 2.0, H-2′), 9.05, 9.15, 9.26 (1H, br.s, each, 3-OH, 3′-OH, 4′-OH), 12.45 (1H, s, 5-OH).

Acid hydrolysis of **5** produced quercetin and D-glucose.

Acetylation of **5** by acetic anhydride in pyridine isolated the octa-acetyl derivative with mp 192-194°C, the mass spectrum of which contained the molecular ion with *m*/*z* 770 and strong peaks for fragments of the tetra-acetylhexose with *m*/*z* 331, 271, 229, and 169 [2, 3, 7].

Flavonoids **1**-**5** are isolated for the first time from *L. lucidus*.

REFERENCES

1. *Plant Resources of the USSR. Flowering Plants, Their Chemical Composition and Use. Hippuridaceae-Lobeliaceae Families* [in Russian], Nauka, St. Petersburg (1991).
2. L. K. Klyshev, V. A. Bandyukova, and L. S. Alyukina, *Plant Flavonoids* [in Russian], Nauka, Alma-Ata (1978).
3. T. J. Mabry, K. R. Markham, and M. B. Thomas, *The Systematic Identification of Flavonoids*, Springer-Verlag, Berlin (1970), Chap. V and IX.
4. N. Sh. Kattaev and G. K. Nikonov, *Khim. Prir. Soedin.*, 115 (1973).
5. I. I. Chemesova and A. L. Budantsev, *Khim. Prir. Soedin.*, 287 (1994).
6. Sh. V. Abdullaev, A. Sattikulov, E. Kh. Batirov, Yu. V. Kurbatov, and V. M. Malikov, *Khim. Prir. Soedin.*, 104 (1983).
7. T. K. Chumbalov, O. V. Fadeeva, and T. K. Nikishchenko, *Khim. Prir. Soedin.*, 89 (1974).