FLAVONOIDS OF THE AERIAL PART OF *Lycopus lucidus*

A. Malik,[1] M. P. Yuldashev,[2] A. Obid,[1] T. Ismoil,[1] and L. Ya. Ping[1]

UDC 547.972

In continuation of research on flavonoids of *Lycopus* L. plants, we studied the phenolic components of *L. lucidus* Turcz. ex Benth (shiny bugle weed). Chrysoeriol, luteolin, quercetin, cinaroside, and quercimeritrin have previously been isolated from the ethylacetate fraction of its aerial part [1].

Chromatography of the butanol fraction (42.0 g) over a silica-gel column using a $CHCl_3$—CH_3OH gradient (95:5-80:20) produced luteolin, quercetin, cinaroside, and flavonoids **1**-**3**. The isolated flavonoids were identified using UV, IR, mass and PMR spectra in addition to chemical transformations and comparison with authentic samples.

Thermopsoside (1) (chrysoeriol-7-O-β-D-glucoside), $C_{22}H_{22}O_{11}$, mp 173-175°C. UV spectrum (EtOH, λ_{max}, nm): 255, 269, 349. IR spectrum: 3460-3270 cm^{-1} (OH); 2930 (methoxy); 1665 (carbonyl γ-pyrone); 1615, 1505 (aromatic C=C); and 1090, 1035 (C–O glycoside).

PMR spectrum (300 MHz, DMSO-d_6 + CCl_4, δ, ppm, J/Hz): 3.05-3.85 (sugar), 3.95 (3H, s, OCH_3), 5.00 (1H, d, J = 7.0, H-1″), 6.45 (1H, d, J = 2.0, H-6), 6.65 (1H, d, J = 2.0, H-8), 6.80 (1H, s, H-3), 6.95 (1H, d, J = 8.0, H-5′), 7.48 (1H, dd, J = 2.0, J = 8.0, H-6′), 7.80 (1H, d, J = 2.0, H-2′), 9.25 (1H, br.s, 4′-OH), 12.85 (1H, s, 5-OH).

Acid hydrolysis of **1** produced chrysoeriol (5,7,4′-trihydroxy-3′-methoxyflavone, $C_{16}H_{12}O_6$, mp 335-337°C, $[M]^+$ 300) and D-glucose [2-4].

Isoquercitrin (2) (quercetin-3-O-β-D-glucoside), $C_{21}H_{20}O_{12}$, mp 236-238°C. UV spectrum (EtOH, λ_{max}, nm): 255, 265 sh, 360; +CH_3COONa, 272, 378; +CH_3COONa/H_3BO_3, 260, 374; +$AlCl_3$, 272, 434; +$AlCl_3$/HCl, 267, 402; +CH_3ONa, 271, 410.

IR spectrum: 3350, 3450 (OH); 1665 (carbonyl γ-pyrone); 1590, 1550, 1510 (aromatic C=C); and 1095, 1045, 1020 (C–O glycoside).

PMR spectrum (300 MHz, DMSO-d_6 + CCl_4, δ, ppm, J/Hz): 3.05-3.90 (sugar), 5.15 (1H, d, J = 7.0, H-1″), 6.15 (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′), 7.55 (2H, dd, J = 2.0, J = 8.0, H-2′, H-6′), 12.45 (1H, s, 5-OH).

Acid hydrolysis produced quercetin (3,5,7,3′,4′-pentahydroxyflavone, $C_{15}H_{10}O_7$, mp 312-314°C, $[M]^+$ 302) and D-glucose.

Acetylation of **2** by acetic anhydride in pyridine isolated the octaacetyl derivative with mp 200-202°C, the mass spectrum of which contained a peak for the molecular ion with *m*/*z* 770 and strong peaks for fragment ions of the tetraacetylhexose with *m*/*z* 331, 271, 229, and 169 [2, 3, 5].

Rutin (3) (quercetin-3-O-rutinoside), $C_{27}H_{30}O_{16}$, mp 193-195°C. UV spectrum (EtOH, λ_{max}, nm): 259, 267 sh, 360, +CH_3COONa, 271, 390; +CH_3COONa/H_3BO_3, 260, 383; +$AlCl_3$, 273, 430; +$AlCl_3$/HCl, 270, 401; +CH_3ONa, 272, 411.

PMR spectrum (300 MHz, DMSO-d_6 + CCl_4, δ, ppm, J/Hz): 1.12 (3H, d, J = 6.0, CH_3), 3.00-4.20 (sugar), 5.03 (1H, br.s, H-1‴), 5.23 (1H, d, J = 7.0, H-1″), 6.16 (1H, d, J = 2.0, H-6), 6.36 (1H, d, J = 2.0, H-8), 6.83 (1H, d, J = 8.0, H-5′), 7.53 (2H, dd, J = 2.0, J = 8.0, H-2′, H-6′), 12.46 (1H, s, 5-OH).

Acid hydrolysis of **3** produced quercetin, D-glucose, and L-rhamnose; partial hydrolysis (90% formic acid in cyclohexanol), isoquercetin [2, 3, 5].

Flavonoids **1**-**3** were isolated from *L. lucidus* for the first time.

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. 6, p. 486, November-December, 2002. Original article submitted December 16, 2002.

 0009-3130/02/3806-0612$27.00

REFERENCES

1. A. Malik and M. P. Yuldashev, *Khim. Prir. Soedin.*, 83 (2002).
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, New York (1970).
4. N. Sh. Kattaev and G. K. Nikonov, *Khim. Prir. Soedin.*, 115 (1973).
5. Sh. V. Abdullaev, A. Sattikulov, E. Kh. Batirov, Yu. V. Kurbanov, and V. M. Malikov, *Khim. Prir. Soedin.*, 104 (1983).