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POLYPHENOLIC COMPOUNDS FROM *Larix gmelinii* PHLOEM

S. Z. Ivanova* and V. A. Babkin

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We previously reported the detection in *Larix gmelinii* (Rupr.) Rupr. of the three stilbene compounds astringenin, astringenin-3′-*O*-*β*-D-glucopyranoside, and piceid [1]. In continuation of research on phenolic compounds from *L. gmelinii* phloem, we isolated two compounds (**1** and **2**) from the Et_2O fraction of the EtOAc extract of larch phloem (March 2009, Bada, Khiloks Region, Chitin Oblast) by column chromatography (SiO_2, $CHCl_3$:MeOH with increasing fraction of MeOH from 0 to 100 vol%) using the published scheme [1]. Compound **1** was isolated by rechromatography over silica gel ($CHCl_3$:MeOH gradient with increasing fraction of MeOH to 40 vol%) with subsequent recrystallization from $CHCl_3$:MeOH; compound **2**, by rechromatography over LH-20 (H_2O:MeOH gradient with increasing fraction of MeOH to 40 vol%). Fractions were analyzed by TLC on Silufol plates using eluents C_6H_6:acetone (3:1) (a) and $CHCl_3$:MeOH (9:1) (b) with detection by $AlCl_3$ and diazotized sulfanilic acid. The yields of **1** and **2** were 0.005 and 0.006%, respectively, of the absolute dry phloem mass.

Compound **1** was classified as a *trans*-stilbene according to its UV spectrum because a strong band with two maxima in the range 300–325 nm was observed. The molecular weight (228) was obtained by mass spectrometry. This suggested that **1** was resveratrol. Resveratrol, like the stilbenes listed above, was not detected previously in the genus *Larix*. Therefore, its identification was confirmed by several spectral methods.

The UV spectrum of **2** exhibited two bands characteristic of flavanones [2 (spectra No. 144, 146, 153)]. These were a strong band with a maximum at 288 nm and a shoulder at 332 nm. Based on the UV spectrum and the molecular weight of 288, **2** was assumed to be eriodictyol. This assumption was also confirmed by several spectral methods because, according to the literature, several difficulties arise with the identification of eriodictyol due to the possible alternate location of the hydroxyls, solvent effects, and other factors [3].

The structures of **1** and **2** were established by IR, UV, and NMR spectroscopy and mass spectrometry. UV spectra were taken on a Perkin–Elmer Lambda 35 UV/Vis spectrometer; IR spectra, a Bruker Vertex 70 in KBr pellets (2.5 mg/300 mg KBr). PMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument at operating frequency 400 and 100 MHz, respectively. Mass spectra were obtained on a Shimadzu GCMS-QP5050A instrument by direct sample introduction at ionization energy 70 eV. Elemental analyses of the compounds agreed with those calculated. Rotation angle was determined on a Polamat A instrument (GDR).

***trans*-Resveratrol (1)**, white granules, $C_{14}H_{12}O_3$, MW 228, mp 249–250°C (CH_3Cl:CH_3OH), lit [4] mp 246°C (CH_3Cl:CH_3OH). UV spectrum (CH_3OH, λ_{max}, nm): 218, 237sh, 306, 320 (log ε 4.40, 4.20, 4.49, 4.48). IR spectrum (KBr, ν, cm^{-1}): 3272 (OH), 1606, 1588 (Ar), 965 (*trans*-CH=CH). PMR spectrum [$(CD_3)_2CO$, δ, ppm, J/Hz]: 6.28 (1H, t, J = 2, H-4), 6.55 (2H, d, J = 2, H-2, H-6), 6.84 (2H, d, J = 8.6, H-3′, H-5′), 6.88 (1H, d, J = 16.4, H-*α*), 7.02 (1H, d, J = 16.4, H-*β*), 7.42 (2H, d, J = 8.6, H-6′, H-2′). ^{13}C NMR spectrum [$(CD_3)_2CO$, δ]: 103.0 (1C, s, C-4), 105.0 (2C, s, C-2, C-6), 116.7 (2C, s, C-3′, C-5′), 127.1 (1C, s, C-*α*), 129.0 (2C, s, C-2′, C-6′), 129.4 (1C, s, C-*β*), 130.2 (1C, s, C-1), 141.1 (1C, s, C-1′), 158.4 (1C, s, C-4′), 159.8 (2C, s, C-3, C-5).

The spectral data agreed with the literature data for resveratrol [4, 5].

Eriodictyol (2), colorless needles, $C_{15}H_{12}O_6$, MW 288, mp 271°C (aq. CH_3OH); lit. [6] mp 262–265°C (aq. C_2H_5OH), [7] mp 270–272°C (aq. C_2H_5OH), [3] mp 271°C (aq. C_2H_5OH); $[\alpha]_D^{21}$ –182.5° (*c* 0.4, CH_3OH); lit. [3] –3.5° (*c* 0.0232, C_2H_5OH). UV spectrum (CH_3OH, λ_{max}, nm): 230sh, 288, 332 (log ε 4.29, 4.26, 3.50). IR spectrum (KBr, ν, cm^{-1}): 3365 (OH), 1604, 1450, 1158, 1086. PMR spectrum (CD_3OD, δ, ppm, J/Hz): 2.73 (1H, dd, J = 17.3, H-3a), 3.1 (1H, dd, J = 17, 13, H-3b), 5.3 (1H, dd, J = 13, 3, H-2), 5.93, 5.91 (2H, 2d, J = 2, H-6, H-8), 6.82 (2H, s, H-6′, H-5′), 6.95 (1H, s, H-2′).

A. E. Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Russia, Irkutsk, e-mail: babkin@irioch.irk.ru, fte@irioch.irk.ru. Translated from *Khimiya Prirodnykh Soedinenii*, No. 1, pp. 109–110, January–February, 2011. Original article submitted June 30, 2010.

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^{13}C NMR spectrum (CD_3OD, δ): 42.7 (C-3), 79.4 (C-2), 94.9 (C-8), 95.8 (C-6), 102.0 (C-10), 113.4 (C-2′), 115.0 (C-5′), 118.0 (C-6′), 130.4 (C-1′), 145.1 (C-3′), 145.5 (C-4′), 163.5 (C-5), 164.0 (C-9), 167.0 (C-7), 196.5 (C-4). The spectral data agreed with the literature data for eriodictyol [3].

Eriodictyol was observed for the first time in phloem of the genus *Larix*. We were unable to find eriodictyol in bark although it is a structural component of the two spirobiflavonoids larixidinol and larisinol, which were identified in bark of *L. gmelinii* and *L. sibirica* [8, 9]. Eriodictyol was found previously in larch wood [10].

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