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LARISINOL, A NEW SPIROBIFLAVONOID FROM *Larix gmelinii* BARK

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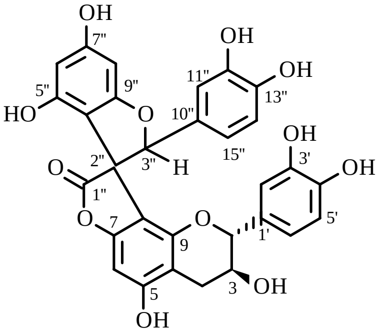
We reported earlier on the observation in bark of Siberian (*Larix sibirica* Ledeb.) and Gmelin larch [*L. gmelinii* (Rupr.) Rupr.] of three representatives of a new class of flavonoids, spiroflavonoids, larixinol, larixidinol, and triflarixinol [1-4]. In continuation of research on flavonoids from Gmelin larch bark, we isolated a new spirobiflavonoid **1**, which we called larisinol.

Larisinol was obtained from the fraction of the ethylacetate extract of larch bark (March 2005, Bada, Khilok Region, Chita District) that contained spirobiflavonoids by column chromatography (SiO_2, $CHCl_3$:CH_3OH, gradient of increasing CH_3OH from 0 to 100 vol. %) using the published method [1]. Rechromatography (flash chromatography, SiO_2, $CHCl_3$:CH_3OH) of this fraction isolated a substance (20 vol. % CH_3OH) enriched in larisinol. Acetylation of the substance (Ac_2O, C_6H_5N) and isolation of larisinol acetate (**1a**) was carried out as before [1]. The structure of the total acetate of larisinol [mp 120-125°C, amorph. (from C_6H_{12})] was established by IR and NMR spectroscopy. IR spectra in KBr disks (2.5 mg/300 mg KBr) were obtained on a Specord 75IR instrument. PMR and ^{13}C NMR in $CDCl_3$ were recorded on a Bruker DPX 400 instrument at working frequency 400 and 100 MHz, respectively. Signals in the PMR and ^{13}C NMR were assigned using two-dimensional HMQC, HMBC, COSY, and NOESY spectroscopy.

The spirane system of benzofuran-type spiroflavonoids with a γ-lactone ring showed characteristic spectral features. The IR spectrum of these compounds and their derivatives had a strong carbonyl absorption band at about 1810-1785 cm^{-1}. The ^{13}C NMR had diagnostic signals at 176-179 ppm belonging to the carbonyl C of the γ-lactone ring (C-1″); at 90.6-91.0 ppm, the methine C atom (C-3″) bound to oxygen of the second heterocycle; at 59.6-61.1 ppm, to the quaternary C atom of the spiro group (C-2″) [1-4].



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The IR ($\nu_{C=O}$ 1810-1770 cm^{-1}) and PMR and ^{13}C NMR spectra of **1a** (Table 1) showed that this compound was a spiroflavonoid. Based on spectral data for larisinol, it was assigned structure **1**. It was found that larisinol was a stereoisomer of the spirobiflavonoid vitisinol, which was isolated from seeds of *Vitis amurensis* Rupr. [5]. Larisinol is in fact a derivative of eriodictyol and (+)-catechin whereas vitisinol is derived from eriodictyol and (-)-epicatechin.

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TABLE 1. PMR and ^{13}C NMR Spectra of **1a**

Atom	^{13}C, δ, ppm	^{1}H, δ, ppm (J/Hz)	Atom	^{13}C, δ, ppm	^{1}H, δ, ppm (J/Hz)
2	77.8	4.46 (d, 8.3)	1″	175.8	
3	68.4	4.78 (m)	2″	59.6	
4	29.7	2.79 (dd, 16.4, 5.3) 2.45 (dd, 16.4, 8.8)	3″	90.6	6.16 (s)
5	150.5		4″	115.0	
6	98.5	6.61 (s)	5″	146.9	
7	150.3		6″	109.8	6.66 (d, 1.8)
8	109.3		7″	152.9	
9	150.8		8″	102.3	6.60 (d, 1.8)
10	110.2		9″	161.2	
1′	135.0		10″	134.2	
2′	121.9	6.88 (d, 2.3)	11″	120.6	6.93 (d, 2.3)
3′	141.4		12″	141.6	
4′	141.9		13″	141.8	
5′	122.9	7.13 (d, 8.3)	14″	123.6	6.96 (d, 8.6)
6′	124.1	6.66 (dd, 8.3, 2.3)	15″	123.1	6.84 (dd, 2.3, 8.6)
			*CH_3CO	19.9-21.1	1.88-2.30 (8 signsls)
			CH_3*CO	165.9-169.6 (8 signals)	

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