FLAVONOIDS FROM *Vaccinium axillare* LEAVES

G. Ya. Mechikova,[1] T. A. Stepanova,[1] A. I. Kalinovskii,[2] L. P. Ponomarenko,[2] and V. A. Stonik[2]

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Plants of the genus *Vaccinium* L. are well known as sources of valuable food and medicinal raw material. For example, compounds isolated from various parts of ordinary bilberry (*V. myrtillus* L.) possess antioxidant [1], vasoprotective, and anti-inflammatory properties [2] and induce apoptosis in tumor cells [3]. Earlier pharmacological investigations of *V. axillare* Nakai showed promise for the use of its extracts in treating sugar diabetes [4]. Flavonoids are known to have a significant positive pharmacotherapeutic effect for this disease [5]. We isolated the flavonoid fractoin and identified its major components because the chemical composition of *V. axillare* has not previsouly been studied.

Leaves of *V. axillare* were collected in Khabarovsk Krai and Sakhalin District in summer 2006. Ground air-dried leaves were successively extracted with 95 and 70% EtOH at 60-70°C. The combined extract was evaporated to an aqueous residue and filtered. The aqueous residue was successively treated with hexane and $CHCl_3$. Then the total phenolic compounds were extracted with EtOAc from the aqueous layer. The EtOAc extract was chromatographed over polyamide (Woelm, Germany) in $CHCl_3$ with added MeOH (from 0 to 10%). The isolated compounds were recrystallized from MeOH and studied using UV, NMR (^{1}H and ^{13}C, DEPT, COSY, HSQC, HMBC), mass spectrometry, and chemical methods (acid hydrolysis). This identified quercetin [6], quercetin-3-*O*-β-D-galactopyranoside (hyperoside) [6], quercetin-3-*O*-α-L-arabinopyranoside [7], and quercetin-3-*O*-α-L-arabinofuranoside (avicularin) [8].

The widely distributed flavonoids quercetin and hyperoside were previously observed in plants of the genus *Vaccinium* L. [9, 10]. However, quercetin-3-*O*-α-L-arabinopyranoside and quercetin-3-*O*-α-L-arabinofuranoside (avicularin) were found for the first time in plants of this genus.

Quercetin-3-*O*-α-L-arabinopyranoside, mp 172-174°C, $[\alpha]_D^{28}$ –65.3° (*c* 0.075, MeOH), lit. [7] $[\alpha]_D^{20}$ –53.96° (*c* 1, MeOH). MALDI-TOF mass spectrum (+) (*m/z*): 457 $[M + Na]^+$, 303 $[algycon + H]^+$. UV spectrum (MeOH, λ_{max}, nm): 257, 267sh, 305sh, 359; ($AlCl_3$) 275, 303sh, 430; ($AlCl_3$ + HCl) 270, 302sh, 346sh, 405; (CH_3ONa) 273, 330sh, 408; (CH_3COONa) 274, 323sh, 375; (H_3BO_3 + CH_3COONa) 262, 300sh, 378. IR spectrum (cm^{-1}): 3400-3300 (OH), 1655 (γ-pyrone C=O), 1607, 1560, 1508 (arom. C=C).

PMR spectrum (CD_3OD, δ, ppm, J/Hz): 7.73 (d, J = 2.2, H-2′), 6.86 (d, J = 8.5, H-5′), 7.56 (dd, J = 8.5, 2.2, H-6′), 6.20 (d, J = 2.0, H-6), 6.39 (d, J = 2.0, H-8), 5.15 (d, J = 6.5, H-1Ara), 3.89 (dd, J = 6.6, 8.4, H-2Ara), 3.64 (dd, J = 8.4, 3.2, H-3Ara), 3.83 (m, H-4Ara), 3.80 (m, H-5Ara), 3.43 (dd, J = 13.4, 3.1, H-5′Ara) [5].

^{13}C NMR spectrum (DMSO-d_6, δ, ppm, $\delta_{DMSO\text{-}d_6}$ = 39.5 ppm): 122.1 (s, C-1′), 115.7 (d, C-2′), 144.9 (s, C-3′), 148.5 (s, C-4′), 115.3 (d, C-5′), 120.9 (d, C-6′), 156.3 (s, C-2), 133.7 (s, C-3), 177.5 (s, C-4), 161.5 (s, C-5), 98.6 (d, C-6), 164.1 (s, C-7), 93.5 (d, C-8), 156.3 (s, C-9), 103.9 (s, C-10), 101.4 (d, C-1Ara), 70.7 (d, C-2Ara), 71.6 (d, C-3Ara), 66.0 (d, C-4Ara), 64.3 (t, C-5Ara).

Avicularin, mp 181-183°C, lit. [8] mp 178°C, $[\alpha]_D$ –156.2° (*c* 0.064, MeOH), lit. [8] $[\alpha]_D^{25}$ –152° (*c* 0.00125, MeOH). MALDI-TOF mass spectrum (+) (*m/z*): 457 $[M + Na]^+$, 303 $[aglycon + H]^+$. UV spectrum (MeOH, λ_{max}, nm): 257, 266sh, 300sh, 356; ($AlCl_3$) 276, 301sh, 431; ($AlCl_3$ + HCl) 272, 299sh, 367sh, 404; (CH_3ONa) 272, 330sh, 403; (CH_3COONa) 263, 321sh, 372; (H_3BO_3 + CH_3COONa) 261, 299sh, 376. IR spectrum (cm^{-1}): 3400-3300 (OH), 1654 (γ-pyrone C=O), 1606, 1550, 1508 (arom. C=C).

1) GOU VPO Far-East State Medical University of Roszdrav, 680000, Khabarovsk, ul. Murav′eva-Amurskogo, 35, e-mail: rec@mail.fesmu.ru; 2) Pacific Institute of Bioorganic Chemistry, FED RAS, 690022, Vladivostok, prosp. 100-Letiya Vladivostoka, 159, fax 7-(4232) 31 40 50, e-mail: stonik@piboc.dvo.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 78-79, January-February, 2008. Original article submitted August 7, 2007.

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PMR spectrum (CD_3OD, δ, ppm, J/Hz): 7.52 (d, J = 2.1, H-2′), 6.89 (d, J = 8.3, H-5′), 7.48 (dd, J = 8.3, 2.2, H-6′), 6.20 (d, J = 2.1, H-6), 6.38 (d, J = 2.1, H-8), 5.46 (d, J = 1.0, H-1Ara), 4.32 (dd, J = 1.1, 3.0, H-2Ara), 3.90 (dd, J = 2.8, 5.2, H-3Ara), 3.86 (m, H-4Ara), 3.50 (m, 2H-5Ara).

^{13}C NMR spectrum (CD_3OD, δ, ppm): 123.1 (s, C-1′), 116.8 (d, C-2′), 146.4 (s, C-3′), 149.8 (s, C-4′), 116.4 (d, C-5′), 123.0 (d, C-6′), 159.3 (s, C-2), 134.9 (s, C-3), 180.0 (s, C-4), 163.1 (s, C-5), 99.9 (d, C-6), 166.0 (s, C-7), 94.7 (d, C-8), 158.6 (s, C-9), 105.6 (s, C-10), 190.5 (d, C-1Ara), 83.3 (d, C-2Ara), 78.7 (d, C-3Ara), 88.0 (d, C-4Ara), 62.5 (t, C-5Ara).

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