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GLUCOSIDE OF TAXIFOLIN AND (+)-PINITOL FROM *Pinus sylvestris*

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Common pine (*Pinus sylvestris* L.) is widely distributed in all forested regions of Siberia and comprises the principal mass of Siberian forests [1]. Pine needles are used as an antiscorbutic agent. Pine buds are used for inhalation for inflammatory diseases of the upper respiratory tract. Pine is rich in ascorbic acid (up to 0.3%) and contains up to 5% tanning agents and up to 1.3% essential oil, the composition of which includes pinene, borneol, limonene, bornylacetate, cadinene, and other terpenes in addition to sterols, terpenoids, alkylated phenols, phenolic acids, alcohols, aldehydes, ketones, stilbenes, lignans, and other aromatic compounds [1, 2, 7–9]. Needles yielded kaempferol; quercetin; quercetin-3-*O*-glucoside; sylpin; derivatives of kaempferol, quercetin, isorhamnetin, and taxifolin 3-*O*-glucosides acylated on the carbohydrate part; taxifolin and eriodictyol 3′-*O*-*β*-D-glucopyranosides; and other flavonoids [3–9].

We studied chemical components of *P. sylvestris* needles in order to discover biologically active compounds of KMAO-Yugry plants. Dried and ground raw material was extracted at room temperature with EtOH (85%). The combined extract was evaporated *in vacuo*, diluted with H_2O, and extracted successively with hexane, $CHCl_3$, EtOAc, and *n*-BuOH. Chromatography of the EtOAc fraction over a column of silica gel using a gradient of $CHCl_3$:EtOH afforded phenolic compound **1**; the *n*-BuOH fraction, **2**.

Compound 1, slightly yellow crystals, $C_{21}H_{22}O_{12}$, $[\alpha]_D^{20}$ –24.6° (*c* 0.4, Me_2CO). PMR spectrum (δ, ppm, J/Hz): 3.00–3.76 (carbohydrate protons), 4.55 (1H, d, J = 11.1, H-3), 4.71 (1H, d, J = 6.6, H-1″), 5.03 (1H, d, J = 11.1, H-2), 5.88 (1H, br.s, H-6), 5.91 (1H, br.s, H-8), 6.85 (1H, d, J = 8.2, H-5′), 7.04 (1H, br.d, J = 8.4, H-6′), 7.26 (1H, br.s, H-2′), 11.93 (1H, br.s, 5-OH).

IR, UV and PMR spectral data indicated that **1** was a glycoside of dihydroflavonol [10–12]. Acid hydrolysis produced an aglycon of formula $C_{15}H_{12}O_7$ [λ_{max} 289, 325 (sh) nm] and D-glucose. The aglycon was identified as taxifolin [(2*R*,3*R*)-dihydroquercetin] based on UV, PMR, and ^{13}C NMR spectra and a comparison with an authentic sample [10, 11]. The ^{13}C NMR spectrum (recorded in off-resonance mode in DMSO-d_6) of **1** showed resonances for C atoms of *β*-D-glucopyranose and taxifolin at 60.6 (C-6″), 69.7 (C-4″), 73.2 (C-2″), 75.9 (C-5″), 77.1 (C-3″), 102.1 (C-1″), 82.9 (C-2), 71.3 (C-3), 197.7 (C-4), 163.2 (C-5), 96.0 (C-6), 166.9 (C-7), 95.0 (C-8), 162.4 (C-9), 100.3 (C-10), 128.2 (C-1′), 115.5 (C-2′), 147.2 (C-3′), 144.9 (C-4′), 116.6 (C-5′), 122.8 ppm (C-6′).

The C-4′ resonance underwent a strong-field shift, those of C-3′ and C-5′, weak-field shifts, upon going from taxifolin to glycoside **1** [10]. Therefore, the glucose was bonded to the hydroxyl in the 4′-position of taxifolin and **1** was taxifolin 4′-*O*-*β*-D-glucopyranoside [12].

Compound 2, $C_7H_{14}O_6$, $[\alpha]_D^{22}$ +65.63° (EtOH), did not absorb in the UV region. Its IR spectrum contained absorption bands at 3600–3250 (OH), 2300–2950 (aliphatic C–C), and 1175 cm^{-1} (C–O). Acetylation of **2** produced a pentaacetyl derivative, the mass spectrum of which showed peaks for ions with *m*/*z* 404 (3%) $[M]^+$, 345 (2), 285 (2), 243 (8), 182 (35), 150 (50), etc.

The PMR spectrum exhibited resonances for methoxyl protons at 3.72 ppm; five protons of a cyclohexane ring geminal to an OH group at 4.76 (d, J = 6.5 Hz), 4.81 (d, J = 4.5 Hz), 5.02 (d, J = 2.1 Hz), 4.93 (d, J = 2.1 Hz), 4.63 (d, J = 5.6 Hz); and one proton geminal to a OCH_3 group at 3.31 ppm (t, J = 9.4, 9.1 Hz).

The ^{13}C NMR spectrum (taken in off-resonance mode in DMSO-d_6) showed resonances for six methine C atoms of a cyclohexane ring bonded to an oxygen at 70.0 (C-3), 70.8 (C-1), 71.9 (C-5), 72.4 (C-2), 72.6 (C-4), 83.8 (C-6) and a resonance for a methoxy C at 59.6 ppm.

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Compound **2** was identified as (+)-pinitol based on the spectral data and a comparison with an authentic sample [13, 14]. (+)-Pinitol was patented in the USA as a hypolipidemic agent [14].

Taxifolin 4′-*O*-*β*-D-glucopyranoside and (+)-pinitol were isolated from *P. sylvestris* for the first time.

REFERENCES

1. A. V. Pobedinskii, *Pine* [in Russian], Lesnaya Promyshlennost′, Moscow, 1979, 125 pp.
2. T. A. Goncharova, *Encyclopedia of Medicinal Plants* [in Russian], Vol. 2, Izdatel′skii Dom MSP, Moscow, 2004, p. 28.
3. S. A. Medvedeva, S. Z. Ivanova, N. A. Tyukavkina, and G. G. Zapesochnaya, *Khim. Prir. Soedin.*, 650 (1977).
4. G. G. Zapesochnaya, S. Z. Ivanova, S. A. Medvedeva, and N. A. Tyukavkina, *Khim. Prir. Soedin.*, 193 (1978).
5. G. G. Zapesochnaya, S. Z. Ivanova, S. A. Medvedeva, and N. A. Tyukavkina, *Khim. Prir. Soedin.*, 332 (1978).
6. S. Z. Ivanova, G. G. Zapesochnaya, N. A. Tyukavkina, and S. A. Medvedeva, *Khim. Prir. Soedin.*, 399 (1978).
7. W. Oleszek, A. Stochmal, P. Karolewski, A. M. Simonet, F. A. Macias, and A. Tava, *Biochem. Syst. Ecol.*, **30**, 1011 (2002).
8. K. Sunnerheim-Sjoberg, G. Eriksson, L. N. Lundgren, and O. Theander, *Scand. J. Forest Res.*, **7**, 325 (1992).
9. T. Popoff and O. Theander, *Acta Chem. Scand., Ser. B*, **31**, 329 (1977).
10. K. R. Markham, *Techniques of Flavonoid Identification*, London, 1982, 113 pp.
11. Y. L. Li, J. Li, N. L. Wang, and X. S. Yao, *Molecules*, **13**, 1931 (2008).
12. X. Xu, H. Xie, J. Hao, Y. Jiang, and X. Wei, *J. Agric. Food Chem.*, **59**, 1205 (2011).
13. A. A. Drenin, E. Kh. Botirov, and Yu. P. Turov, *Khim. Rastit. Syr′ya*, No. 2, 53 (2010).
14. L. N. Misra and S. A. Siddiqi, *Curr. Sci.*, **87**, 1507 (2004).