A C-GLYCOSIDE FROM THE NEEDLES OF Larix sibirica

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From a methanolic extract of the needles of Larix sibirica Ledb. (Siberian larch) by chromatography on polyamide powder and elution with water, we have isolated a compound with mp 203-205°C (methanol), $[\alpha]_D^{20}$ −69.14° (c 0.38; methanol). The absorption in the UV region at 270, 334 nm (log ε 4.30, 4.31) and the frequency of the stretching vibrations of the C=O group in the IR spectrum (1654 cm^{-1}) show the flavone structure of the substance.

In the PMR spectrum, ring A is represented by a singlet at δ 6.33 ppm, for which the proton at C_6 is responsible. The signal at δ 13.22 ppm is due to the proton of the 5-OH group participating in a strong intramolecular hydrogen bond.

The para-substituted phenyl side chain of ring B is confirmed by deformation vibrations (818, 842 cm^{-1}) in the IR spectrum. The PMR spectrum has doublets at δ 8.12 and 7.0 ppm (J = 7 Hz) corresponding to the H-2', H-6' and the H-3', H-5' protons, respectively. The bathochromic shifts in the UV spectra in the presence of the corresponding salt additives show the presence of free OH groups in positions 4', 5, and 7.

The absence in the PMR spectrum of a signal due to a proton at C_8 permits the assumption that the compound under investigation is a C-glycoside. Acid hydrolysis with 10% HCl gave a compound differing chromatographically from the initial compound, with mp 262-264°C, but having the same IR and UV spectra as the initial compound. The elementary composition and melting point of this material and a comparison with an authentic sample showed that it was vitexin. A hydrolyzate was shown to contain rhamnose by descending paper chromatography [butan-1-ol–pyridine–water (6:4:3)]. The presence of rhamnose was also shown by GLC of the substance in the form of the aldononitrile acetate [1].

A signal at δ 5.28 ppm is due to a proton at C' of the glucose substituent and a signal at δ 5.05 ppm to a proton at C'' of the rhamnose.

The PMR spectrum described above was recorded in dimethyl sulfoxide, the same solvent being used as internal standard. Consequently, in this spectrum it was impossible to detect the signals of the methyl group of the rhamnose residue. In the PMR spectrum of the glycoside under investigation in deuteromethanol, a doublet (J = 6 Hz) belonging to the CH_3 group of rhamnose appeared at δ 0.58 ppm. The remaining 11 protons of the glucose and rhamnose residues are resolved in the δ 3.0-3.80-ppm region.

Thus, the compound isolated is a rhamnosylvitexin [2]. The nature of the bond between the rhamnose and the glucose is being determined.

It is interesting to note that until now no C-glycosides have been found in the needles of plants of the family Pinaceae. Only recently has a brief communication appeared on the detection of two C-glycosides in the needles of Larix laricina [3]. The PMR spectra were taken on a BS 487B with dimethyl sulfoxide and hexamethyldisiloxane as internal standards. The solvents were dimethyl sulfoxide and deuteromethanol. The chemical shifts are given relative to the signal of hexamethyldisiloxane.

The GLC analysis was performed in the carbohydrate laboratory of the Institute of Biologically Active Substances, Far-Eastern Scientific Center, Academy of Sciences of the USSR on a Tswett-2 instrument under the conditions given in a previous paper [1].

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LITERATURE CITED

1. V. A. Khomenko, A. F. Pavlenko, T. F. Solov'eva, and Yu. S. Ovodov, Khim. Prirodn. Soedin., 393 (1971).
2. V. S. Batyuk, Khim. Prirodn. Soedin., 288 (1966).
3. I. J. Niemann and R. Bekooy, Phytochem., 10, 893 (1971).