ASTRAGALIN FROM THE NEEDLES OF Larix sibirica

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UDC 547.972.35

From a methanolic extract of the needles of Larix sibirica (Siberian larch) by chromatography on polyamide and elution with 30% aqueous methanol we have isolated a fraction containing three substances. The chromatography of this fraction on polyamide in a nonaqueous system [chloroform–methanol (95 : 5)] yielded an individual compound with mp 173-175°C (methanol), $[\alpha]_D^{20}$ −23.01° [c 0.25; methanol–water (1 : 1)].

The UV absorption at 267 and 350 nm (log ε 4.28, 4.20, 4.24, 4.33)* and the frequency of the stretching vibrations of the C=O group in the IR spectrum (1660 cm^{-1}) show the flavonoid structure of the compound. In the NMR spectrum, two doublets (δ = 6.28 and 6.50 ppm, J = 2.6 Hz) correspond to two protons at C_6 and C_8 of ring A. The lateral phenyl ring is para-substituted. This is shown by the bands of the deformation vibrations in the IR spectrum (810, 840 cm^{-1}) and by two doublets (δ = 6.98 and 8.11 ppm) in the NMR spectrum. The constant J = 9.0 Hz corresponds to the interaction of the protons at C_2, and C_3, and those at C_5, and C_6, which are in the ortho positions with respect to one another. A signal at δ 12.68 ppm is due to the proton of a 5-OH group, the presence of which is also confirmed by a bathochromic shift of the long-wave maximum by 44 nm in the presence of $AlCl_3$. A broad singlet (width 60 Hz) with its center at δ = 9.82 ppm is due to the protons of the 4'-OH and 7-OH groups, leading to a displacement of the short-wave maximum by 8 nm and of the long-wave maximum by 19 nm in the UV spectrum in the presence of sodium acetate.

A signal at δ = 5.49 ppm relates to the protons of a glycosidic substituent. The β configuration of the glycosidic aglycone–sugar bond was shown by hydrolysis with β-glucosidase.

Acid hydrolysis gave the aglycone, with mp 269-272°C (aqueous methanol) with a yield of 61%, which corresponds to a monoglycoside.

In the NMR spectrum of the aglycone there is no signal at δ = 5.49 ppm. The doublets corresponding to the protons at C_6 and C_8, at C_2' and C_6', and at C_3' and C_5' agree with the corresponding signals of the protons in the spectrum of the glycoside. The appearance of a free 3-OH group on hydrolysis is satisfactorily confirmed by the increase in the bathochromic shift in the presence of $AlCl_3$ in the UV spectrum of the aglycone as compared with the spectrum of the glycoside (55 nm). Consequently, the aglycone is 3,4',5,7-tetrahydroxyflavone (kaempferol).

The hydrolysate was shown to contain glucose by paper chromatography [butanol–pyridine–H_2O (10 : 3 : 3)].

The experimental results that we have obtained permit the compound isolated to be characterized as kaempferol 3-glucoside (astragalin), which has been found in the flowers of Aesculus hippocastanum L. [1].

The NMR spectra were taken by V. K. Voronov on a BS487B spectrometer. Dimethyl sulfoxide was used as solvent and as internal standard. The values of the chemical shifts are given relative to the signal of hexamethyldisiloxane.

*As in Russian original – Publisher.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, p. 123, January-February, 1972. Original article submitted November 3, 1971.

LITERATURE CITED

1. L.Hörhammer, H. J. Gehrmann, and L. Endres, Arch. Pharm., 262/64, 3, 113 (1959).