A LIGNAN GLYCOSIDE FROM THE NEEDLES OF Pinus sibirica

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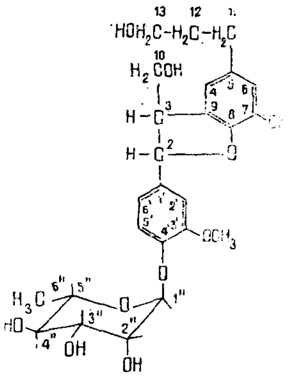
The detection of lignan glycosides in the needles of some species of conifers of Siberia and the Far East has been reported previously [1]. We give the results of an investigation of lignan glycosides of the needles of the siberian stone pine Pinus sibirica R. Mayr.

The butanol fraction of a methanolic extract of the needles was chromatographed on polyamide with water in order to obtain the total lignan glycosides. They were separated by chromatography on silica gel using benzene-methyl ethyl ketone mixtures with increasing concentrations of the latter from 50 to 100% as eluents. The compounds were purified by repeated rechromatography under the same conditions. Compound (I), isolated in an amount of 0.08% on the absolutely dry needles, coincided in its chromatographic behavior with 7-hydroxy-2(4'-hydroxy-3'-methoxyphenyl)-3-hydroxymethyl-5-(γ-hydroxypropyl)-[1]-benzofuran 4'-O-rhamnopyranoside.

The structure of this compound which has here been isolated from Siberian stone pine needles for the first time, was confirmed with the aid of chemical and spectral methods of analysis. It consisted of an amorphous slightly yellowish powder readily soluble in polar solvents: alcohols, water, acetone. On being heated to 100°C with 5% HCl for 30 min it hydrolyzed with the formation of rhamnose and a series of aromatic compounds arising as a result of the instability of the aglycone in an acid medium.

The UV and IR spectra gave general information on the structure of the compound and indicated its aromatic nature: $\lambda_{\max}^{CH_3OH}$ 280 nm (log ε 2.76); $\lambda_{\max}^{KBr}$ 1500, 1600 cm^{-1}, and the presence of an OH group was shown by a bamd at 3400-3500 cm^{-1} and that of ether bonds by absorption at 1000-1200 cm^{-1}. We used the ^{13}C NMR method to establish the structure of (I). The spectrum contained 12 signals of sp^2-hybridized carbon atoms of aromatic rings in the 110-150 ppm region and 13 signals of sp^3-hybridized carbon atoms of the carbohydrate moiety of the molecule and of the propane chains in the 17.8-101 ppm region. The assignment of the ^{13}C chemical shifts of the signals was made on the basis of an analysis of the spectra with incomplete decoupling from protons and by analogy with literature information given for compounds having similar fragments [2, 3] (D_2O, XL-200 spectrometer; s - singlet; d - doublet; q - quartet; m - multiplet in the spectra with incomplete decoupling from protons):



C atom No.	Chemical shift, ppm	C atom No.	Chemical shift, ppm
12	32,2(s)	9	1[illegible],2(s)
11	35,[illegible](s)	1'	136,0(s)
3	54,8(s)	5	137,6(s)
OCH_3	56,0(q)	8	140,8(s)
13	61,6(s)	4'	146,0(s)
10	64,4(s)	7	14[illegible],0(s)
2	86,2(d)	3'	151,2(s)
2'	110,4(d)	6''	17,8(m)
6	116,7(d)	5''	6[illegible],6(d)
5'	116,8(d)	3''	71,2(d)
4,	118,4(d)	2''	72,1(d)
6	119,2(d)	4''	73,6(d)
		1''	100,6(d)

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The study of the lignan glycosides of pine needles is continuing.

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COUMARINS FROM THE HERBAGE OF TURKMENIAN SPECIES OF THE GENUS *Achillea*

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In an investigation of the herbage of two species of the genus *Achillea* (*A. biebershteinia* Afan. and *A. krasheninnikovii*) from the family *Asteraceae* collected in the flowering period in the environs of Nokhur village, Bakharden region, Turkmen SSR, substances of a benzo-α-pyrone nature have been isolated. A series of substances fluorescing blue and green-blue in UV light was detected by paper chromatography.

To isolate these substances, the herbage of *Achillea biebershteini* was extracted with a tenfold amount of 95% ethanol and the ethanolic extract was evaporated until the solvent had been eliminated completely, after which the residue was treated with distilled water (1:2) and the aqueous solution was extracted successively with chloroform, diethyl ether, and ethyl acetate.

The chloroform extract (fraction 1) was evaporated and the residue was tranferred to a column of polyamide (1:30). Elution was performed with benzene and the with benzene—chloro-fomrm and benzene—ethanol.

The extraction and separation of the substance from *Achillea krasheninnikovii* were performed similarly.

As a result three substances were isolated from the chloroform fraction of these plants.

Substance (I) = $C_9H_3O_6$, mp 228-230°C. From its physicochemical properties it was identified as umbelliferone (7-hydroxycoumarin) In UV light it fluoresced bright blue [1].

Substance (II) - $C_{10}H_8O_4$, mp 204-205°C. On the basis of its physicochemical properties and those of its acetyl derivatives and their UV spectra, this compound was identified as scopoletin [2].

Substance (III) had the empirical formula $C_{10}H_8O_4$. In view of the identical elementary composition and close R_f values in a number of solvent systems of the substance isolated and scopoletin, it was assumed that this substance was an isomer of scopoletin — 6-hydroxy-7-methoxycoumarin.

The subsequent methylation of esculin with dimethyl sulfate showed that substance (III) was identical with 6-hydroxy-7-methoxycoumarin [3].

Thus, from the epigeal parts of *A. biebersteinii* and *A. krasheninnikovii* we have isolated the hydroxycoumarine, umbelliferone, scopoletin, and isoscopoletin for the first time. The structures of the substances isolated were confirmed by the results of UV and IR spectroscopy and acid and alkaline hydrolyses, and also by comparison with authentic samples.

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