BRIEF COMMUNICATIONS

HYDROXYSTILBENES OF THE INNER AND OUTER BARK OF *Picea ajanensis*

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Stilbene compounds are found in the bark of the representatives of the family Pinaceae only in the cases of the genera *Pinus* [1, 2] and *Picea* [3-7]. Continuing an investigation of the bark of the genus *Picea*, from a methanolic extract of the inner bark (phloem) of the Jeddo spruce, by a method described previously [7], we have isolated two stilbene compounds which have been identified as 3,3',4',5-tetrahydroxystilbene (astringenin) and its 3-β-D-glucopyranoside (astringin) [5, 6].

Astringenin (I), consisted of crystals in the form of white needles with mp 219-220°C (methanol—chloroform). UV spectrum of (I): λ_{max} (methanol) 220, 235, 305, 325 nm (log ε 4.32, shoulder; 4.29; 4.36). IR spectrum, cm^{-1}: 3330 (OH), 1604, 1520 (C_6H_5). Mol. wt. 244 (by mass spectrometry).

The acetate of (I) formed white prisms with mp 118-120°C (ethyl acetate—petroleum ether). UV spectrum: λ_{max} (methanol) 210, 232, 302, 312, 326 nm (log ε 4.32, 4.30, 4.51, shoulder). IR spectrum, cm^{-1}: 1762 (acetate C=O), 1611, 1592 (C_6H_5). The permanganate oxidation of the acetate of (I) yielded protocatechuic and α-resorcylic acids, which were identified by the GLC method in the form of their TMS esters [8].

Astringin (II) consisted of white needles with mp 219-220°C (methanol—chloroform), $[\alpha]_D^{22}$ —65.4° (c 2.63; acetone). UV spectrum of (II): λ_{max} (methanol) 220, 237, 305, 328, 343 nm (log ε 4.50, 4.37, 4.46, shoulder). IR spectrum, cm^{-1}: 3443 (OH), 1610, 1592 (C_6H_5).

The acetate of (II) formed white needles with mp 149-150°C (methanol—water), $[\alpha]_D^{22}$ —23.0° (c 2.0; acetone). UV spectrum: λ_{max} (methanol) 208, 229, 299, 307 nm (log ε 4.46, 4.21, 4.49, 4.49). IR spectrum, cm^{-1}: 1760 (acetate C=O), 1590, 1510 (C_6H_5). According to mass spectrometry (mol. wt. of the acetate of (II) 700), compound (II) is a monoglycoside.

From the products of the hydrolysis of astringin (in the form of the acetates) we isolated the aglycone and showed it to be identical with the acetate of (I). D-glucose was identified by the PC method, and its β-pyranose form was shown by hydrolysis with *Aspergillus oryzae* and by calculation of the molecular rotation.

The acetate of (II) was hydrolyzed, and the aglycone obtained was methylated and oxidized by the usual method [3]. The identification in the products of 5-hydroxy-3-methoxybenzoic acid showed that the glucose was attached to position 3.

The stilbenes isolated have the trans configuration, as was confirmed by the frequency of the deformation vibrations of the CH groups of the double bond and by the position of the absorption maxima in the UV spectrum [7].

By the GLC of the TMS ethers, 3,4',5-trihydroxystilbene (resveratrol) and 3,4',5-trihydroxy-3'-methoxystilbene (isorhapontigenin) were identified in the phloem of the yellow spruce, and resveratrol and astringenin in the outer bark.

Astringenin and astringin are the main stilbene compounds of the phloem of yellow spruce (1.0 and 1.5%, respectively, on the absolutely dry weight). Other stilbenes are present in

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it in considerably smaller amounts. The predominating stilbene component of the outer bark is astringenin.

Student O. I. Fomina took part in the work.

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