BRIEF COMMUNICATIONS

HYDROXYSTILBENES OF THE PHLOEM OF Picea koraensis

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An aqueous methanolic (1 : 1) extract of the phloem of Picea koraensis Nakai (Korean spruce) after the elimination of the methanol by distillation was treated successively with chloroform (to extract waxes) and with diethyl ether. By chromatography on impregnated silica gel [1], from the ether-soluble fraction we isolated a compound (I), and by a combination of chromatography on polyamide and impregnated silica gel, from the ether-insoluble fraction we isolated a compound (II). Because of the lability of these compounds all the experimental operations with them were performed in an atmosphere of CO_2 (with traces of SO_2) [2]. For the same reason, to perform a number of chemical reactions we used the acetate protection of the hydroxy groups of these compounds.

Compound (I), $C_{15}H_{14}O_4$, mp 182-183°C (ethyl acetate–petroleum ether). UV spectrum: λ_{max} (methanol) 219, 235, 303, 327, 342 nm (log ε 4.32, 4.42, 4.32, 4.41, shoulder); IR spectrum: 3350 (OH), 2850 (OCH_3), 1610, 1520 cm^{-1} (C_6H_5).

The acetate of (I) had mp 103-104°C (ethyl acetate–petroleum ether). UV spectrum: λ_{max} (methanol) 211, 233, 303, 312, 325 nm (log ε 4.31, 4.26, 4.42, 4.42, shoulder); IR spectrum: 1770 (acetate C=O), 1619, 1516 cm^{-1} (C_6H_5). Permanganate oxidation [3] of the acetate of (I) gave vanillic and α-resorcylic acids, which were identified by the GLC method in the form of their TMS esters [4]. These results show that compound (I) is 3,4',5-trihydroxy-3'-methoxystilbene (isorhapontigenin).

Compound (II), mp 193-194°C (methanol–chloroform), $[\alpha]_D^{22}$ −53.4° (c 2.24; acetone). UV spectrum: λ_{max} (methanol) 219, 235, 307, 325, 345 nm (log ε 4.48, 4.37, 4.45, 4.56, shoulder); IR spectrum: 3350 (OH), 2900 (OCH_3), 1600, 1590, 1520 cm^{-1} (C_6H_5).

The acetate of (II) with the composition $C_{33}H_{36}O_{15}$ had mp 163°C (ethyl acetate–petroleum ether). UV spectrum: λ_{max} (methanol) 211, 234, 305, 315 nm (log ε 4.29, 4.42, 4.42, shoulder); IR spectrum: 1752 (acetate C=O), 1516, 1605 cm^{-1} (C_6H_5).

By hydrolyzing it with the enzyme of Aspergillus oryzae we identified glucose, the β-pyranose form of which was confirmed by calculating the value of the molecular rotation [5]. The aglycone of compound (II) is isorhapontigenin.

The site of attachment of the carbohydrate residue was determined by analyzing the products of the permanganate oxidation of the acetate of (II): the isolation of glucosidated α-resorcylic acid showed the attachment of the glucose in position 3 of the isorhapontigenin. Thus, compound (II) was identified as 3,4',5-trihydroxy-3'-methoxystilbene 3-O-β-D-glucopyranoside (isorhapontin).

Both compounds were in the trans form, as was confirmed by the frequency of the deformation vibrations of the double bond (960-970 cm^{-1}) and by the position of the UV absorption maxima (303, 327 nm) [6].

The glycoside of isorhapontigenin is present in predominating amount. By analytical chromatography the extract from the phloem of the Korean spruce was found to contain small amounts of another two stilbene compounds – astringenin and resveratrol. The presence of isorhapontigenin and its glycoside, isorhapontin, is characteristic for the bark of other species of Picea [7, 8].

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