HYDROXY- AND OXOMATAIRESINOLS FROM PICEA OBOVATA

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By preparative chromatography on a polyamide solvent (Kapron from the Barnaul combine) in a water–methanol system, we have isolated from an acetone extract of the wood of Picea obovata (Siberian spruce) two phenolic compounds which we have called A and B.

Substance A. $C_{20}H_{22}O_7$, white powder with mp 124–125° C (benzene), $[\alpha]_D^{20}$ −13° (c 3.0, tetrahydrofuran), mol wt 373 (ebullioscopic) and giving an orange coloration with Pauly's reagent. The substance absorbs at 282 mμ (log ε 3.88), which is characteristic for the benzene ring. The IR spectrum (in a tablet with KBr) has absorption bands at (cm^{-1}) 1750 (carbonyl of a lactone group), 1465, 1518, and 1605 (aromatic nucleus), and also bands at 1155, 1210, and 1240, which are typical for guaiacyl structures [1]. The isolation of vanillin from the nitrobenzene oxidation of substance A confirms the presence of a guaiacyl fragment.

The acetate of substance A, $C_{26}H_{28}O_{10}$, is an amorphous powder, decomp. p. 96–98° C (ethanol–water), $[\alpha]_D^{20}$ +15.6° (c 1.64, tetrahydrofuran). UV spectrum (ethanol): λ_{max} 275 mμ (log ε 3.48). The IR spectrum lacks absorption bands of stretching vibrations of a hydroxyl group.

The analytical results show that substance A is a dimer of a guaiacylpropane structure containing a hydroxyl group in the aliphatic part of the molecule. In actual fact, the IR spectrum taken in chloroform solution (c 0.01 M) shows bands of phenolic and aliphatic hydroxyls (3605 and 3545 cm^{-1}, respectively).

Substance A is unstable on storage in the air, and on chromatography in a thin layer of silica gel it changes, giving several spots. The oxidation of this substance in formic acid led to a compound giving a pink color with Pauly's reagent which we identified as conidendrin [2]. The ready formation of the tetralin ring can be explained by the presence of a hydroxyl group in the α-position with respect to the benzene ring [3, 4]. The investigation performed has shown that substance A is hydroxymatairesinol.

Substance B forms small white crystals with mp 71–72° C (water–ethanol), λ_{max} (in ethanol) 230 and 282 mμ (log ε 4.09 and 4.33). The IR spectrum has bands at (cm^{-1}) 1465, 1520, and 1595 (C_6H_5—), 3420 (OH group), 2855 (—OCH_3), 1622 (ketone carbonyl), and 1755, 1755 [sic] cm^{-1} (lactone carbonyl). With Pauly's reagent it gives a red-violet color, and nitrobenzene oxidation forms vanillin. The results of a comparison of the chromatographic behavior of this compound with an authentic sample confirmed that it is oxomatairesinol.

The instability of hydroxy- and oxomatairesinols in a weakly acid medium complicates working with them on silica gel. We have repeatedly observed that, during separation in a thin layer of silica gel, authentically individual hydroxymatairesinol gives two or three spots. The eluate from the chromatographic layer is acidic (pH 4.5), which probably causes various transformations of the lignanes. Consequently, their successful isolation and purification were achieved only by the use of a neutral polyamide sorbent.

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