LIOVIL FROM Abies sibirica AND Picea obovata

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The hydroxyaromatic extractive of spruce and fir are guaiacyl and guaiacylpropane derivatives with various degrees of oxidation [1]. We have previously isolated vanillin (Picea obovata, Abies sibirica) [2] and the lignans conidendrin and hydroxy- and oxomatairesinols (Picea obovata) [3].

The present paper describes the preparation of methanolic and acetonic extracts of fir (1) and spruce (2), which were percolated on cellulose powder (petroleum ether, benzene, chloroform, acetone, methanol, water). The combined chloroformic and acetonic eluates were chromatographed on columns of various solvents. For the extract (1) we used polyamide with benzene–methanol (95 : 5) as the eluent and silica gel with benzene–ethyl acetate (1 : 1) as the eluate, and for (2) we used the eluent benzene–chloroform–methanol (22 : 14 : 2). The chromatographic separation of both extracts gave individual substances which were shown to be identical with one another and which we have called B_1.

Substance B_1 forms colorless needles with the composition $C_{20}H_{24}O_7$, mp 162-164°C (from methanol, 165-167°C, (from acetone), $[\alpha]_D^0$ −33.5° (c 2.79; methanol), mol. wt. 376 (mass spectrometry). The substance absorbs at λ_{max} 280 nm (log ε 5.09; ethanol) and the presence of a phenolic hydroxy group is confirmed by a bathochromic shift of the long-wave band in an alkaline medium (λ_{max} 298 nm, log ε 4.07; ethanol + NaOH) and by a positive reaction (orange color) with diazotized sulfanilic acid. In the IR spectrum (with KBr), there are characteristic absorption bands at (cm^{-1}): 1605, 1520, 1460 (aromatic system), 3330-3490 (associated hydroxyls), and 1270, 1235, and 1035 (ether bonds), which are typical for the guaiacyl structure, which is confirmed by the formation of vanillin in the nitrobenzene oxidation of compound B_1. The hydrogenation of B_1 over $PdCl_2$ forms an amorphous product giving a red coloration with diazotized sulfanilic acid. This change in coloration may be connected with the disappearance of hydroxy groups present in the para position to a guaiacyl hydroxyl [1].

Acetylation yielded a substance in the form of an amorphous powder with the composition $C_{28}H_{32}O_{11}$, decomposition temperature 66-68°C (from ethanol), mol. wt. 542.8 (ebullioscopy).

The IR spectrum of the acetate has bands at 1740 and 1760 cm^{-1} and the PMR spectrum (in deuterochloroform) has singlets at 1.98 and 2.2 ppm showing the presence of aliphatic and aromatic acetoxy groups. The IR spectrum showed that acetylation had taken place completely.

The experimental results enabled substance B_1 to be identified as the lignan compound liovil. A chromatographic comparison and a mixed melting point with authentic liovil given to us by Prof. Weinges confirmed their identity.

This is the first time that liovil has been obtained from Abies sibirica.

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