LIGNAN COMPOUNDS FROM THE WOOD OF *Larix dahurica* AND *L. sibirica*

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We have previously studied the flavonoid composition of the extractive substances of the wood of the Dahurian and Siberian larches [1-3]. The successive treatment of the total extract (500 g) from the wood of the Dahurian larch with anhydrous acetone, dry chloroform, and petroleum ether gave a mixture of phenolic substances insoluble in petroleum ether (8 g). By chromatography on a column of silica gel in the chloroform–ethyl acetate (15:1) system, a fraction of lignan compounds (3 g) containing six components was isolated. By hot-water extraction, this fraction yielded compound A (1.9 g), and the residue, by chromatography on a column of alumina in butan-1-ol–benzene systems (proportion of butanol successively 3, 5, 20, 40, and 60 vol. %) containing 10% of water, yielded compound B (0.4 g).

On oxidation with nitrobenzene, both substances gave vanillin, which shows that they have the guaiacyl structure [4].

Substance A formed white crystals, $C_{20}H_{26}O_6$, with mp 112-113°C (ether), $[\alpha]_D^{20}$ −29.2° (c 0.26; dioxane); λ_{max} (ethanol) 232, 282 nm (log ε 4.31, 4.05. IR spectrum, cm^{-1}: 1455, 1520, 1610 (C_6H_5–); 1390, 2850 (–OCH_3); 3430 (associated OH groups) (in KBr); 3540 (phenolic OH groups) and 3610 (aliphatic OH groups) (in $CHCl_3$). Substance A was identified as secoisolariciresinol.

Substance B formed colorless crystals, $C_{20}H_{24}O_5$, mp 116-116.5°C (methanol); $[\alpha]_D^{20}$ −50.8° (c 0.31; dioxane); λ_{max} (ethanol) 233, 282 nm (log ε 4.23, 3.92). IR spectrum, cm^{-1}: 1470, 1522, 1614 (C_6H_5–), 1380, 2850 (–OCH_3), 3540 (phenolic OH groups) (in KBr and $CHCl_3$).

Substance B was identified as 3,4-divanillyltetrahydrofuran. On being heated in methanolic solution in the presence of 10% HCl in a sealed tube in the water bath for 10 h, the secoisolariciresinol (64 mg) was converted completely into its anhydride – 3,4-divanillyltetrahydrofuran.

After the isolation of compounds A and B from the lignan fraction, the remaining four components were identified by the method of chromatographic depression in thin layers of silica gel [heptane–chloroform–ethyl acetate (1.5:2:3; 2:4:3); hexane–chloroform–methanol (1:2:2; 11:7:2)] and Al_2O_3 [heptane–ethyl acetate (1.5:1); benzene–ethyl acetate–dioxane (49:8:3); hexane–ethyl acetate–dioxane (39:1:8)] as conidendrin, pinoresinol, lariciresinol, and isolariciresinol. In a fresh extract, the lariciresinol predominated among these components. In extracts stored for a long time, the isolariciresinol was present in greater amount. Lariciresinol is capable of ready isomerization into isolariciresinol in hydrochloric acid (pH 2.0) or formic acid (pH 1.0) at room temperature.

The extract of the wood of the Siberian larch contained similar lignan compounds.

The literature contains reports of the isolation of secoisolariciresinol [5] and conidendrin [6] from extracts of the wood of L. decidua and of lariciresinol [7] from wound resin of this species [7]. This is the first time that pinoresinol, isolariciresinol, and 3,4-divanillyltetrahydrofuran have been isolated from Siberian species of larch.

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