AROMADENDRIN, APIGENIN, AND KAEMPFEROL FROM THE WOOD OF Pinus sibirica

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During the chromatographic isolation of chrysin, tectochrysin [1], pinostrobin, and pinocembrin [2] from acetone extracts of the wood of Pinus sibirica (Siberian pine) we observed the presence of very small amounts of more highly hydroxylated flavonoids. To accumulate these substances, we obtained fractions enriched in them (treatment with solvents, percolation on cellulose and polyamide). After repeated preparative separation on polyamide (eluents: chloroform–methanol; methanol–water), three compounds were isolated which gave a positive cyanidin test and were aglycones (according to Bryant's reaction [3]). The substances were identified as aromadendrin, apigenin, and kaempferol. It is interesting to note that in Erdtman's fundamental paper [4] on the composition of the phenolic components of the genus Pinus the three flavonoids mentioned were found in none of the 65 species studied.

Aromadendrin: white crystals with mp 227-230° C (from water), $[\alpha]_D^{20}$ + 22.6° (c 0.31; methanol), mol. wt. 288 (mass spectrometry). IR spectrum (in KBr; cm^{-1}): 1520,1610 (C_6H_5–), 1640 (C = O), 3300, 3450 (–OH). UV spectrum, λ_{max}, nm: 292, 330 (shoulder) (log ε 4.31) (ethanol); 308 (+$AlCl_3$); 330 (+CH_3COONa); 320 (+$ZrOCl_2$); 290 (+ citric acid).

The reduction of the substance according to Pew [5] gave a purple coloration, while alkaline cleavage with 30% NaOH at 100° C for 6 h yielded phloroglucinol and oxidation under the conditions described by Hillis [6] yielded kaempferol. The acetate of aromadendrin has mp 78-80° C (from ethanol).

The optical rotatory dispersion (ORD) curve had a complex Cotton effect in which the troughs of a positive effect corresponding to a transition at 325 nm and of a negative effect with a center at 288 nm intersect one another. This becomes obvious on comparing the ORD and the circular dichroism curves (Fig. 1). Since the ORD curve of aromadendrin has a positive effect corresponding to a $n \rightarrow \pi^*$ transition and a negative effect corresponding to a $\pi \rightarrow \pi^*$ transition, the configuration of the compound isolated is 2(R):3(R) [7, 8]. This conclusion is confirmed by the PMR spectrum. The signal of the proton at C_2 consists of a doublet in the 5.05 ppm region and that at C_3 a doublet at 4.5 ppm. The spin-spin coupling constant of 11 Hz corresponds to the axial position of the protons at C_2 and C_3, i.e. the C_6H_5 and OH subtituents are in the equatorial positions, which also corresponds to the 2(R):3(R) configuration.

Apigenin: pale yellow crystals with mp 343-344° C, mol. wt. 270 (mass spectrometry). IR spectrum, cm^{-1}: 1550, 1610 (C_6H_5 –), 1655 (C = O), 3090, 3300 (–OH). UV spectrum: λ_{max} 340, 270 nm (log ε 4.37, 4.35) (ethanol).

Kaempferol: lemon-yellow crystals with mp 275-276° C, IR spectrum, cm^{-1}: 1515, 1570, 1615 (C_6H_4 –), 1652 (C = O), 3200 – 3400 (–OH). UV spectrum: λ_{max} 370, 268 nm (log ε 4.31, 4.23) (ethanol).

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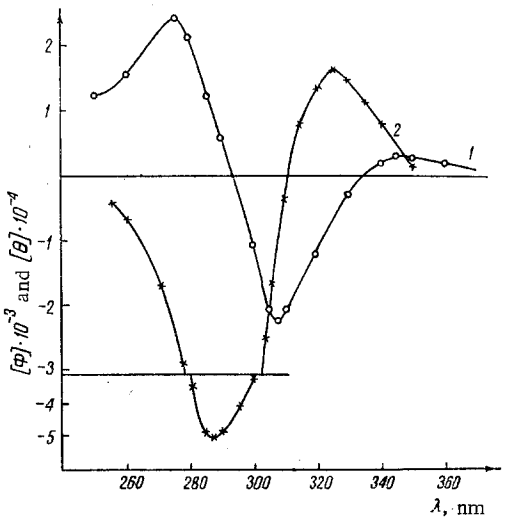

Fig. 1. ORD (1) and CD (2) curves of aromadendrin in methanol.

The ORD and circular dichroism curves were taken on a "Spectropol 1" instrument by V. A. Babkin and the PMR spectra on a Varian A-60 instrument in dimethyl sulfoxide (with hexamethyldisiloxane as internal standard).

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