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HYDROXYSTILBENES OF PINUS SIBIRICA AND PINUS SILVESTRIS

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In a study of the extractive substances of a phenolic nature from the heartwood of Pinus sibirica (Siberian pine) and Pinus silvestris (Scotch pine) growing in the Irkutsk Oblast, we have isolated two substances of a stilbene nature: pinosylvin (I) and its monomethyl ether (II). The isolation of substance (II) from Siberian pine has been reported previously [1, 2]. The presence of these substances is characteristic for the genus Pinus [3]. It is known that they increase the resistance of the wood to rotting and complicate the process of cooking wood-pulp cellulose [4].

Compound	Mp, °C	Absorption in the UV region, mμ				Fluorescence, mμ	
		λ_{max}	log ε	λ_{max}	log ε	λ_{max}	I_{rel}
I	155–156	228	4.25	303	4.44	410	1.0
II	120–121	235	4.20	300	4.22	410	0.93
Dimethyl ether of (I)	56–57	230	4.18	300	4.16	410	0.21
Diacetate of (I)	99–101	230	4.18	300	4.36	—	—
Acetate of (II)	65–66	228	4.00	300	4.16	—	—

An acetone extract obtained from heartwood chips was separated into ether-soluble and ether-insoluble fractions. The first of them was chromatographed on polyamide sorbent with gradient elution by mixtures of chloroform and methanol. The table gives the characteristics of the pinosylvin and its monomethyl ether that were isolated, and also of their methyl and acetate derivatives. The results of elementary analysis and the determination of the molecular weights by mass spectrometry coincide with the calculated figures. For all the compounds given in the table, the IR spectra contained absorption bands at 1505, 1600 (1590), and 1616 cm^{-1} (benzene ring and C=C bond), 690 cm^{-1} (monosubstituted benzene ring), and 865, 840, and 820 cm^{-1} (1, 3, 5-substituted benzene ring). The presence of a band at 965 cm^{-1} confirms the trans-structure of the compounds studied. This is also shown by a comparison of the nature of the absorption of these compounds in the UV region with that for trans-stilbene (λ_{max} 297 and 228 mμ, log ε 4.45 and 4.20). [5].

An analysis of the absorption in the UV region of the five stilbene derivatives has shown that the introduction into the stilbene system of such electron-donating substituents as OH, $OCOCH_3$, and OCH_3 does not lead to a shift in the absorption maxima of stilbene but lowers their intensity. Thus, the replacement of hydroxyl by the more strongly nucleophilic methoxy group in the sequence (I) → (II) → dimethyl ether of (I) leads to the following decrease in the intensity of absorption expressed as log ε: 4.44 → 4.22 → 4.16.

Pinosylvin and its mono- and dimethyl ethers have their maximum fluorescence at the same wavelength but differ in the relative intensity of the fluorescence, which falls on passing from pinosylvin to the monomethyl and, especially, to the dimethyl ether.

REFERENCES

1. A. I. Lisina, L. N. Vol'skii, E. F. Kalistratova, and V. A. Pentegova, Izv. SO AN SSSR, ser. khim., no. 6, 113, 1967.
2. N. A. Tyukavkina, V. I. Lutskii, A. K. Dzizenko, and V. A. Pentegova, KhPS, [Chemistry of Natural Compounds], 4, 249, 1968.
3. H. Erdtman, Bot. Mag., Tokio, 79, 499, 1966.
4. H. Erdtman, Ann., 539, 116, 1939.
5. H. Erdtman, Svensk Kem. Tidskr., 56, 134, 1944.

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