

POLYPHENOLS OF THE BARK OF *Larix sibirica*T. K. Chumbalov, L. T. Pashinina,
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In the isolation of the flavonoids [1] from the bark of *Larix sibirica* Ledeb. (Siberian larch) previously defatted with benzene, the acid-containing fractions were separated off and in them eight phenolic acids were detected by two-dimensional paper chromatography in the solvent systems: 1) benzene-acetic acid-water (6:7:3) and 2) sodium formate-formic acid-water (10:1:200). On the basis of qualitative reactions, five of them have been assigned to the group of hydroxycinnamic acids and the remaining three to the hydroxybenzoic acids.

Adsorption chromatography on polyamide sorbent (with ether and methanol as the eluents) gave individual substances (VI) and (VIII). The other fractions each contained two or three acids, which were separated by preparative paper chromatography in system 2 and were purified on KU-2 ion-exchange resin.

From their melting points, UV spectra, equivalents, and a comparison with authentic samples, the phenolic acids under investigation were identified as ferulic acid, trans form (I), λ_{\max} 320 nm, cis form (II), λ_{\max} 298 nm; p-coumaric acid, trans form (III), λ_{\max} 333 nm, cis form (IV), λ_{\max} 290 nm; caffeic acid (V), λ_{\max} 325 nm; vanillic acid (VII); p-hydroxybenzoic acid (VI); and protocatechuic acid (VIII). The trans isomers of the acids (I-IV) showed the characteristic long-wave shift of λ_{\max} in comparison with the cis isomers.

Quantitative determinations of the hydroxybenzoic acids were performed on an SF-4A spectrophotometer from the densities of the spots revealed with diazotized p-nitroaniline and of the hydroxycinnamic acids from the densities of the eluates of the spots in cells with a thickness of the absorbing layer of 1 cm (see Table 1) [2].

The acids found are present in the bark in the free state; the β -glucosides of p-hydroxybenzoic, vanillic, and p-coumaric acids have been found in the needles of the Siberian larch [3].

A concentrated benzene extract was treated with petroleum ether and the part insoluble in petroleum ether was chromatographed on alumina (with ether as the eluent). This gave a white amorphous substance

TABLE 1

Acid	Name of the acid	R _f value in system		Amount, %
		1	2	
I	Ferulic, trans form	0,75	0,28	0,010
II	Ferulic, cis form	0,79	0,68	0,008
III	p-Coumaric, trans form	0,44	0,34	0,011
IV	p-Coumaric, cis form	0,45	0,76	0,007
V	Caffeic	0,08	0,35	0,005
VI	p-Hydroxybenzoic	0,49	0,59	0,025
VII	Vanillic	0,86	0,55	0,008
VIII	Protocatechuic	0,09	0,56	0,006

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with mp 61-62°C. Alkaline hydrolysis with a 20% solution of KOH gave eicosanol, mp 71-72°C and ferulic acid. The results obtained for the compound under investigation and its derivatives correspond to the ester of eicosanol and ferulic acid isolated previously from Larix laricina [4].

LITERATURE CITED

1. T. K. Chumbalov, L. T. Pashinina, and Z. A. Leiman, *Khim. Prirodn. Soedin.*, 478, 764 (1970).
2. T. A. Krupnikova, L. I. Dranik, and V. I. Davydova, *Rast. Res.*, 7, 449 (1971).
3. S. A. Medvedeva, N. A. Tyukavkina, and S. V. Ivanova, *Khim. Prirodn. Soedin.*, 844 (1971).
4. G. K. Nair and E. Rudloff, *Canad. J. Chem.*, 37, 1608 (1959).