PHENOLIC COMPOUNDS OF THE BARK OF Pinus sibirica

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A special place in the group of extractive substances of the bark and wood of coniferous and broad-leaved species is occupied by the polyphenols, many of which possess physiological activity. The phenolic components of the bark of various coniferous species have been studied by a number of authors both in the USSR and abroad [1-6].

The present paper gives the results of the isolation and study of the phenolic compounds of the bark of Pinus sibirica (Siberian pine).

From the ethereal fraction of the bark of the pine, three substances of a flavonoid nature were obtained, On the basis of qualitative reactions, the products of alkaline fusion, characteristic absorption bands in the UV and IR spectra, and comparative chromatography with authentic samples it was established that substance I was identical with taxifolin, II with quercetin, and III with (+)-catechin.

In addition to flavonoids, the ethereal extract contained derivatives of benzoic acid (protocatechuic and vanillic acids) and derivatives of cinnamic acid (p-coumaric, caffeic, and ferulic acids).

EXPERIMENTAL

Samples of the bark of Pinus sibirica were taken in Western Sayan (trial area of the Forestry and Timber Institute of the Siberian Branch of the Academy of Sciences of the USSR).

The dried and comminuted bark was extracted successively with petroleum ether, chloroform, and diethyl ether. Chromatography of the concentrated ethereal fraction showed that it consisted of a large number of individual components. The polyphenolic compounds were separated by adsorption chromatography on polyamide [7]. Elution was performed with water and mixtures of water and ethanol with increasing concentrations of ethanol. The eluates were studied by chromatography on paper [type B ("fast") of the Leningrad Volodarskii mill]. The following systems of solvents were used: 1) 2% acetic acid; 2) butan-1-ol–27% acetic acid (1 : 1); 3) phenol–water (73 : 27); 4) butan-1-ol–acetic acid–water (4 : 1 : 2); and 5) propanol–ammonia (70 : 30).

TABLE 1. Properties of the Aromatic Acids of Pine Bark

Substance	Coloration with		R_f in systems			Acid
	diazotized sulfanilic acid	p-nitroaniline	1	4	5	
IV	Lilac	Cherry-red	0,42	0,86	0,26	Protocatechuic
V	Orange	Dark violet	0,46	0,92	0,40	Vanillic
VI	Pink	Brownish-violet	0,30	0,92	0,46	p-Coumaric
VII	Faint yellow	Yellow-brown	0,28	0,86	0,36	Caffeic
VIII	Violet	Brown	0,20	0,88	0,48	Ferulic

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The IR spectra of the substances were taken on an IKS-14 spectrometer and the UV spectra on an SF-4A spectrophotometer with complex-forming and ionizing reagents. The molecular weights were determined by the Rast method of fusion with camphor.

Substance I, $C_{15}H_{12}O_7$, mp 240-242°C (from 50% aqueous ethanol) crystallized out in the form of fine colorless needles.

Substance II, $C_{15}H_{10}O_7$, had mp 311-313°C (from 30% ethanol).

On the basis of the UV spectra, the bathochromic shifts, and the products of hydrolysis, these substances were identified as dihydroquercetin and quercetin, respectively.

Substance III, $C_{15}H_{14}O_6$, mp 170-171°C, crystallized from water in the form of small needles, R_f 0.31 (1), 0.42 (3), 0.65 (4). With a 1% solution of vanillin in hydrochloric acid it gave a pink-red coloration. UV spectrum: λ_{max} (ethanol) 200 nm (log ε 3.62). IR spectrum, cm^{-1}: 3472, 3300 (OH), 1600, 1495 (C_6H_5).

The pentaacetate of (III) had mp 132-133°C. The experimental information obtained enabled this compound to be identified as 3,3',4',5,7-pentahydroxyflavan(catechin).

By preparative chromatography on paper, the ethereal extract yielded five other compounds. On the basis of qualitative reactions, two of them were shown to belong to the hydroxybenzoic acid group and the remaining three to the hydroxycinnamic acid group. Characteristic qualitative reactions, UV spectroscopy, and comparative chromatography with markers in several systems of solvents (see Table 1) made it possible to identify the first two compounds as protocatechuic acid (IV) and vanillic acid (V) and the last three as p-coumaric acid (VI), caffeic acid (VII), and ferulic acid (VIII).

The hydroxycinnamic acids are present in the bark in the free state, which is confirmed by their IR spectra: for (VI) λ_{max} (ethanol) 300 nm; (+ sodium acetate) 286; (+ sodium ethoxide) 335; (+ boric acid + sodium acetate) 280; (+ aluminum chloride) 305; for (VII) λ_{max} (ethanol) 326, 330; (+ sodium acetate) 308, 287; (+ sodium ethoxide) 358, 250; (+ boric acid + sodium acetate) 318, 297; (+ aluminum chloride) 358, 315, 235 nm; for (VIII) λ_{max} (ethanol) 317, 290; (+ sodium acetate) 308, 290; (+ sodium ethoxide) 342; (+ boric acid + sodium acetate) 308, 290; (+ aluminum chloride) 320 nm.

In the case of all the acids studied, the addition of fused sodium acetate led to a slight hypsochromic shift of the maximum of the first band, while esters of these acids [9] gave a bathochromic shift. As is well known [9], the addition of boric acid and sodium acetate to ethanolic solutions of esters of hydroxycinnamic acids shifts the absorption maximum in the long-wave direction, while in the case of the free acids it causes a hypsochromic shift, and this is confirmed by our results.

SUMMARY

Dihydroquercetin, quercetin, (+)-catechin, and protocatechuic, vanillic, p-coumaric, caffeic, and ferulic acids have been isolated from an ethereal extract of the bark of Pinus sibirica.

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