

BRIEF COMMUNICATIONS

PHENOLIC ACIDS OF THE BARK OF *Pinus*

silvestris, *P. sibirica*, AND *P. abies nephrolepis*

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Acetone extracts of the barks of *Pinus silvestris* L. (Scots pine) and *P. abies nephrolepis* Maxim (whitebark pine) were treated with petroleum ether to eliminate waxy substances and then with diethyl ether in order to extract the polar phenolic components. The phenolic acids were obtained from the etheral fractions by extraction with saturated sodium bicarbonate solution. The phenolic acids from an extract of the bark of *P. sibirica* R. Mayr (Siberian pine) were isolated by a method described previously [1].

The following acids were identified preparatively by the TLC and PC methods in the materials investigated: p-hydroxybenzoic, vanillic, protocatechuic, p-coumaric, and ferulic. Silylated fractions of the phenolic acids were analyzed by GLC on a "Tsvet-4" chromatograph with a flame ionization detector using a 300 × 0.3 cm column containing 5% of SE-30 on Chromaton N-AW-HMDS with helium as the carrier gas at column temperatures of 135, 192, and 234°C and evaporator temperatures of 250-270°C. The trimethylsilyl (TMS) esters [2] were identified by the method of additives and by comparison of the retention times (RTs) with those of authentic samples. The results of the analysis are given in Table 1.

The GLC method showed the presence in extracts of the bark of Scots pine and whitebark pine, in addition to the phenolic acids detected by TLC and PC, of caffeic acid, and the absence of benzoic and syringic acids. Vanillin was also identified in extracts of the bark of Scots pine.

Thus, in the phenolic acids isolated from the bark of the species studied the type of substitution of the benzene ring is characteristic for the family Pinaceae: p-hydroxy, 3,4-dihydroxy, and 4-hydroxy-3-methoxy. To each acid of the cinnamic type corresponds its analog of the benzoic type.

The bark of the whitebark pine contains mainly p-hydroxy-substituted acids - p-coumaric and p-hydroxybenzoic. In the bark of the Scots pine, protocatechuic acid predominates and in the bark of the

TABLE 1. Relative Retention Times (RRTs)* of the TMS Esters of the Phenolic Acids

TMS esters of the following acids	Scots pine		Whitebark		Siberian p.	
	192°	234°	162°	234°	192°	234°
p-Hydroxybenzoic	0,47	—	0,47	—	0,47	—
Vanillic	0,78	—	0,79	—	0,78	—
Protocatechuic	1,00	1,00	1,00	1,00	1,00	1,00
p-Coumaric	—	1,45	—	1,44	—	1,45
Ferulic	—	2,20	—	2,21	—	2,25
Caffeic	—	2,61	—	?	—	2,55

*The RT of the TMS ester of protocatechuic acid was taken as 1.00 at all temperatures.

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Siberian pine, vanillic acid. The considerable amount of vanillic acid in the bark of the Siberian pine confirms the general conclusion on the high level of development of methylating enzyme systems in the subgenus H. aploxylon of the genus Pinus, while the predominance of protocatechuic acid in the bark of the Scots pine is in harmony with the idea of the feeble development of methylating systems in the subgenus diploxylon.

LITERATURE CITED

1. A. S. Gromova, A. I. Syrchina, and N. A. Tyukavkina, *Khim. Pri rodn. Soedin.*, 824 (1971).
2. S. H. Lanher, P. Pantages, and I. Wender, *Chem. Ind.*, 1664 (1958).