to the phloem and rhytidome there are stilbenes that are characteristic for only one type of tissue. Astringin, which has been isolated from the phloem of the Korean spruce, was not found in the rhytidome of this species. Resveratrol trimethyl ether and pinosilvin and its mono- and dimethyl ethers were found only in the rhytidome of the Siberian pine.

In the phloem, the concentration of glycosidated stilbenes is considerably higher than that of free stilbenes, while in the rhytidome the opposite relationship is found.

LITERATURE CITED

1. A. S. Gromova, N. A. Tyukavkina, V. I. Lutskii, G. A. Kalabin, and D. F. Kushnarev, Khim. Prirodn. Soedin., 677 (1975).
2. A. S. Gromova, V. I. Lutskii, and N. A. Tyukavkina, Khim. Prirodn. Soedin., 778 (1974).
3. N. A. Tyukavkina, V. I. Lutskii, A. S. Gromova, and V. K. Voronov, Khim. Prirodn. Soedin., 600 (1972).

PHENOLIC ACIDS OF THE PHLOEM OF *Abies nephrolepis*, *Pinus sibirica*, AND *P. sylvestris*

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We have previously reported the composition of the phenolic acids of the rhytidome of the Khingan fir (*Abies nephrolepis*), Siberian pine (*Pinus sibirica*), and Scotch pine (*Pinus sylvestris*). In the present paper we give the results of an investigation of the phenolic acids of the phloem of these plants.

Evaporated methanolic extracts of Khingan fir, Siberian pine, and Scotch pine were separated by treatment with diethyl ether into two fractions. From the ether-soluble solution by a method described previously [1] we isolated the phenolic acid fractions: p-hydroxybenzoic, vanillic, protocatechuic, p-coumaric, and ferulic acids. From the ether-insoluble extract by preparative chromatography on polyamide we obtained a fraction of glycosidated phenolic acids.

The phenolic acid glycosides were hydrolyzed with 10% HCl. The aglycones proved to be identical with the phenolic acids present in the free state. As the carbohydrate residue we found only glucose. The attachment of the glucose by an ether bond was established by alkaline hydrolysis, and the β configuration of the glycosidic center was found from the results of hydrolysis with emulsin. This shows that the compounds isolated are β-glucosides.

The free phenolic acids and also the products of hydrolytic cleavage of the glycosidated phenolic acids were identified by GLC.

The phenolic acids were analyzed in the form of their trimethylsilyl (TMS) ethers [2] under the following conditions: "Tsvet-4" chromatograph, flame-ionization detecter (FID), stationary phase 5% of SE-30 on Chromaton N-AW-HMDS, column 300 × 0.3 cm, column temperature 215°C, evaporator temperature 260°C, carrier gas helium, rate of flow of helium 1.7 liters/h.

The relative retention times of the TMS ethers of the phenolic acids were: p-hydroxybenzoic 0.56; vanillic 0.80; protocatechuic 1.0; p-coumaric 1.66; ferulic 2.51. The retention time of protocatechuic acid (22.5 mm) was taken as 1.

The glucose was identified in the form of the acetate of the aldononitrile under the following conditions: "Khrom-4" chromatograph, FID, stationary phase 5% of SE-30 on Chromaton N-AW-HMDS, column 250 × 0.3 cm,

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carrier gas nitrogen, rate of flow of nitrogen 1.8 liter/h. The column temperature was programmed linearly from 150 to 220°C at a rate of heating of 5 deg/min. Evaporator temperature 250°C. The glucose issued at 196°C.

The amount of phenolic acids did not exceed 0.02% of the absolutely dry weight of the phloem.

Thus, the pholems of the Khingan spruce, Siberian pine, and Scotch pine contain the set of hydroxybenzoic and hydroxycinnamic acids that is characteristic for coniferous plants. Within each species, the qualitative composition of the free phenolic acids of the phloem and of the rhytidome proved to be similar, with the exception of caffeic acid, found only in the rhytidome of the Scotch pine. Glycosidated phenolic acid was found only in the phloem.

It is an interesting that the presence of glycosidated phenolic acids is characteristic for the phloem of all the species, and the presence of phenolic esters with higher n-aliphatic alcohols for the rhytidome [3].

This is the first time that glycosidated phenolic acids have been found in the bark of the genera Abies and Pinus.

LITERATURE CITED

1. N. A. Tyukavkina, A. S. Gromova, V. I. Lutskii, and I. S. Chubarova, Khim. Prirodn. Soedin., 78 (1974).
2. S. H. Langer, P. Pantages, and I. Wender, Chem. Ind. (London), 1664 (1958).
3. V. G. Leont'eva, A. S. Gromova, V. I. Lutskii, L. D. Modonova, and N. A. Tyukavkina, Khim. Prirodn. Soedin., 240 (1974).

PHENOLIC ACIDS OF Ephedra equisetina

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A concentrated aqueous extract of green sprigs of Mongolian ephedra (Ephedra equisetina) was treated with a 5% solution of sodium bicarbonate and extracted with ethyl acetate and with n-butanol to eliminate phenols. The aqueous fraction was acidified to Congo Red and extracted with ethyl acetate. The ethyl acetate was distilled off to dryness, and the residue was dissolved in water and chromatographed on polyamide with elution by 30% methanol. After concentration of the eluate, a mixture of acids was obtained which was analyzed by paper chromatography and gas-liquid chromatography.

The paper chromatography of this mixture in the systems benzene–acetic acid–water (6 : 7 : 3) and sodium formate–formic acid–water (10 : 1 : 200) and diazotization with p-nitroaniline to reveal the spots showed the presence of four acids: p-hydroxybenzoic, protocatechuic, vanillic, and p-coumaric.

The gas–liquid chromatography of the phenolic acids was performed on a "Khrom 3-1" chromatograph with a flame-ionization detector. Nitrogen was used as the carrier gas at a rate of flow of 25 ml/min. The phenolic acids were separated best in a steel column (0.5 × 0.98 cm) filled with 30/60 mesh glass beads. The liquid phase was Apiezon L (0.05 wt.%), and the column temperature was 210°C and the evaporator temperature 270°C. The acids were analyzed in the form of their methyl ethers by comparing the retention times of known substances and of the components of the acid fraction under investigation and from the increase in the area under a peak with the addition of the corresponding authentic substance. The amounts of the components in the fractions were determined from the areas of the peaks by multiplying the height of each peak by its width at half-height. The relative retention times and amounts of the components in the phenolic acid fraction are given below:

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