## BRIEF COMMUNICATIONS

# STILBENES OF THE RHYTIDOME OF Pinus sibirica AND Picea koraiensis

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We have previously shown that the inner bark (phloem) of the Siberian pine (Pinus sibirica Rupr. Mayr.) [1] and of Korean spruce (Picea koraiensis Nakai) [2] contains a fairly wide assortment of stilbene compounds. In the present paper we give the results of an investigation of the stilbenes from the outer bark (rhytidome) of these species.

In a benzene extract of the rhytidome of the Siberian pine we found the trimethyl ether of resveratrol and pinosylvin and its mono- and dimethyl ethers, and in an acetone extract, in addition to the pinostilbene and resveratrol described previously [3], we found their glycosides – pinostilbenoside and resveratroloside. Of the eight stilbenes of the rhytidome of the Siberian pine the main ones are resveratrol and pinostilbene (0.1 and 0.2% on the absolutely dry weight of the rhytidome); the others are present in trace amounts and therefore their identification proved possible only by GLC.

An aqueous methanolic extract of the Korean spruce was exhaustively treated with diethyl ether. The following stilbenes were identified in the ether-soluble part of the extract by the GLC method: resveratrol, isorhapontigenin, and astringenin, and in the ether-insoluble fraction there were glycosides of resveratrol (piceid) and of isorhapontigenin (isorhapontin).

The GLC analysis of the TMS ethers of the stilbene compounds was performed under the following conditions: I. Stilbenes. "Tsvet-4" instrument, FID, column 300 × 0.3 cm, rate of flow of helium 1.6 liters/h. II. Stilbene glycosides. "Khrom-4" instrument, FID. 1. SE-30, column 250 × 0.3 cm, rate of flow of nitrogen 1.8 liters/h, temperature programmed from 260 to 340°C, rate of heating 5 deg/min. 2. OU-17, column 120 × 0.3 cm, rate of flow of nitrogen 1.65 liter/h, temperature programmed from 260 to 300°C, rate of heating 2 deg/min.

On comparing the chemical compositions of the stilbenes of the phloem and the rhytidome within each species, a number of qualitative and quantitative differences are found. Thus, together with compounds common

TABLE 1. Relative Retention Times and Elution Temperatures of Stilbene TMS Ethers

| Stilbene TMS ether | 5% XE-60 | 5% SE-30 | | 3% |
|---|---|---|---|---|
| | 264° | 246° | 264° | Ou-17 |
| Pinosilvin | 1*—(14 mm) | 1*—(42 mm) | — | — |
| Pinosilvin monomethyl ether | 1,30 | 0,80 | — | — |
| Pinosilvin dimethyl ether | 1,73 | 0,66 | — | — |
| Resveratrol | — | — | 1* (43 mm) | — |
| Resveratrol trimethyl ether | — | — | 0,63 | — |
| Pinostilbene | — | — | 0,90 | — |
| Isorhapontigenin | — | — | 1,43 | — |
| Astringenin | — | — | 1,52 | — |
| Piceid | — | — | 332° | 282° |
| Resveratroloside | — | — | 332° | 289° |
| Pinostilbenoside | — | — | 332° | 291° |
| Isorhapontin | — | — | 338° | 287° |

*Retention time taken as 1.

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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


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# 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 $\beta$ configuration of the glycosidic center was found from the results of hydrolysis with emulsin. This shows that the compounds isolated are $\beta$-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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