PHENOLIC ACIDS AND THEIR GLYCOSIDES FROM THE NEEDLES OF Abies sibirica AND A. nephrolepis

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From methanolic extracts of the needles of Abies sibirica Ledeb. and A. nephrolepis Maxim (Siberian and Khingan firs) by preparative chromatobraphy on a polyamide sorbent we have isolated fractions containing mixtures of phenolic acid glycosides.

We identified the acids obtained by the hydrolysis (10% HCl) of these fractions from the retention times of their methyl derivatives in gas–liquid chromatography [1] (Table 1). The analysis was performed on a "Khrom-3" chromatograph with a flame-ionization detector. Column 1.2 m×6 mm with 15% of silicone DS-550 on Chromaton AW-HMDS (0.25-0.36 mm). The temperature was raised linearly from 150 to 270°C at the rate of 4°C/min.

In view of the fact that on methylation some phenolic acids (vanillic, protochechuic) give the same dimethyl derivative, for their identification we also chromatographed their TMS derivatives [2] (see Table 1) on a "Tsvet-4" chromatograph with a flame-ionization detector at 195 and 228°C, column 3 m×3 mm with 5% of silicone SE-30 on Chromaton AW-HMDS (0.2-0.25 mm).

In the hydrolyzate neutralized on AV-17 anion-exchange resin, by chromatograph [PC, butanol–pyridine–water (6:4:3), butanol–acetic acid–water (4:1:5)] we identified only glucose.

The attachment of the glucose to the phenolic hydroxyl in the glucosides was confirmed by the negative results of alkaline hydrolysis, and the results of enzymatic hydrolysis of the phenolic acid glucosides showed that all the compounds contained a β-glycosidic bond.

Thus, the presence of the β-glucosides of p-hydroxybenzoic, vanillic, protocatechuic, and p-coumaric acids in the needles of A. sibirica Ledeb. and A. nephrolepis Maxim. has been established. Free p-hydroxybenzoic, vanillic, and p-coumaric acids have been detected in A. sibirica Ledeb.

This is the first time that the hydroxybenozic and hydroxycinnamic acids that we have identified have been found in needles of the genus Abies.

TABLE 1. Retention Times (RT's) and Relative Retention Times (RRT's) of Phenolic Acid Derivatives

Phenolic acid	RRT's of methyl deriv. 15% DS-550	RT's of silyl deriv. 5% SE-30
p-Hydroxybenzoic	1,00*	6
Vanillic		9,3
Protocatechuic	1,6	12,1
p-Coumaric		
cis-	1,8	—
trans-	2,1	5,6

* RT = 13.3 min.

LITERATURE CITED

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