GLYCOSIDES OF PHENOLIC ACIDS OF THE NEEDLES OF Larix sibirica

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UDC 547.587

By column chromatography on polyamide, from the total methanolic extract of the needles of Larix sibirica we have isolated an aqueous fraction of glycosides of hydroxyaromatic acids. After hydrolysis with 10% HCl at 95-96°C for 4 h, a mixture of acids was obtained by the usual methods. The paper chromatography of this mixture in the system 2% acetic acid, butan-1-ol – acetic acid – water (4:1:5), and isopropanol – ammonia – water (10:1:1) showed the presence of p-hydroxybenzoic, vanillic, and p-coumaric acids. Both the acids themselves and the cis and trans isomers of p-coumaric acid were separated best in the first of the systems mentioned.

By treatment with diazomethane in diethyl ether – methanol (1:1 by volume) the methyl esters of the mixture of acids isolated from the needles, and also the methyl esters of authentic samples of the acids, were prepared. The methyl esters were analyzed by the GLC method (Khrom-2 chromatograph with a flame-ionization detector, using nitrogen as the carrier gas and silicone SE-30 on Chromosorb W as the stationary phase at a temperature of 180°C). The relative retention times (RRTs) of the methyl esters of the acids from the needles and of standard samples of the acids agreed well (retention time of the standard 11.05 min).

Methyl esters	Relative retention times	
	from the needles	standard samples
p-hydroxybenzoic	1.0	1.0
vanillic	2.18	2.14
p-coumaric		
cis	3.42	3.25
trans	3.74	3.85

The GLC results show that the p-coumaric acid is present in the extract predominantly in the trans form.

Paper chromatography in the systems butanol – pyridine – water (3:3:1) and butanol – acetic acid – water (4:1:5) showed the presence of glucose alone as the carbohydrate residue. The absence of esters was confirmed by negative alkaline hydrolysis.

The enzymatic hydrolysis of the glycosides with dextrinase and β-emulsin showed that all the compounds contained β-glucosidic linkage.

Thus, the β-glucosides of p-hydroxybenzoic, vanillic, and p-coumaric acids have been identified in a methanolic extract of the needles of Larix sibirica. The β-glucosides of vanillic and p-coumaric acids and the α-glucoside of p-hydroxybenzoic acid have been found in the needles of Larix laricina [1].

The GLC analyses were performed in the wood chemistry laboratory of the All-Union Institute of Organic Chemistry of the Siberian Branch of the Academy of Sciences of the USSR.

LITERATURE CITED

1. G. I. Niemann, Phytochem., 8, 2101 (1969).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 6, p. 844, November-December, 1971. Original article submitted June 11, 1971.