PHENOLIC GLYCOSIDES OF THE BARK OF Salix schwerinii

V. A. Kompantsev and V. I. Glyzin

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We have reported previously the isolation from the leaves of Salix schwerinii E. Wolf. of the flavonol glycosides quercitrin, myricitrin, and isorhamnetin 3-rhamnoside [1].

To isolate the phenolic glycosides, the finely cut fresh bark (1.2 kg) with branches of plants aged from 2 to 6 years collected in the Khikhtsir state reservation (near Khabarovsk) was extracted with methanol–ethanol (2 : 1). The resulting extract was concentrated under vacuum at 50-60°C to small volume and the residue was dissolved in three to four volumes of distilled water and was purified with chloroform. The tannin substances and other polyphenolic compounds were precipitated with a 10% solution of basic lead acetate. This precipitate was separated off, and the phenol glycosides were extracted from the aqueous filtrate with ethyl acetate. Then the ethyl acetate extract was evaporated under vacuum to the minimum volume, deposited on a column of cellulose (50 cm high and 7 cm in diameter) and extracted with butan-1-ol–xylene–water (4 : 6 : 8) [2], 50-ml fractions being collected. No phenolic glycosides were found in the first fractions, and in the 25th to 36th a glycoside was eluted with the composition $C_{15}H_{20}O_7$, mp 175-177°C (water-saturated ethyl acetate), $[\alpha]_D^{20} -60°$ (c 1.78; water; length 0.5 dm); mp of the acetate of the glycoside 105-108°C (aqueous methanol); $[\alpha]_D^{20} -35°$ (c 1.14; chloroform; length 0.2 dm).

On careful enzymatic hydrolysis with emulsin by a known method [3] the hydrolyzate was found to contain the aglycone 4-hydroxycinnamyl alcohol, mp 116-118°C (diethyl ether) and D-glucose, which shows the β configuration of the glycosidic bond. The aglycone and the glycoside on chromatograms gave a deep blue coloration with 1% solution of ferric chloride and a dark red coloration with diazotized sulfanilic acid (presence of a free phenolic hydroxyl) [4]. The red coloration of the aglycone and of the glycoside with Millon's reagent shows that the phenolic hydroxyl is in the para position in relation to the first substituent in the benzene ring [2].

The UV spectra of the aglycone and of the glycoside each have one well-defined maximum, at 263 nm (log ε 3.12) and 264 nm (log ε 2.84), respectively. Under the influence of alkali there is considerable bathochromy: in the aglycone by 27 nm (λ_{max} 290 nm) and in the glycoside by 26 nm (λ_{max} 290 nm), which confirms the presence of a free phenolic hydroxyl in the glycoside and in the aglycone [4].

The IR spectrum of the glycoside shows characteristic bands at (cm^{-1}): 1090, 1050, 1020 (vibrations of the pyranose ring of a sugar), 890 (β configuration of the glycosidic bond), 845 (1,4-disubstitution in a benzene ring), 3270 (stretching vibrations of a free phenolic hydroxyl), and 2970 and 2950 (stretching vibrations of aliphatic CH groups).

According to the information given, the phenolic glycoside isolated is 3-(4-hydroxyphenyl)prop-2-en-1-ol 1-O-β-D-glucopyranoside (triandrin) [4].

On continuing the elution of the total phenolic glycosides from the cellulose column, we obtained from fractions 44-55 the glycoside salicin (salignin 2-O-β-D-glucopyranoside), $C_{15}H_{18}O_7$, mp 200-201°C (water-saturated ethyl acetate), $[\alpha]_D^{20} -62°$ (c 1.22; water; length 0.2 dm); UV spectrum ($5 \cdot 10^{-3}$ M solution in absolute ethanol), λ_{max} 268 nm; λ_{max}^{NaOH} 269 nm; mp of the acetate of the glycoside 133-134°C (aqueous methanol), $[\alpha]_D^{20} -23°$ (c 0.99; chloroform; length 0.2 dm) [5].

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