PHENOLIC COMPOUNDS OF *Salix songarica*

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To investigate their flavonoid composition, the dry leaves of *Salix songarica* Anderss. (Dzhungarian willow) [1], collected in the region of Nukus, Karakalpak ASSR, were exhaustively extracted with chloroform in an apparatus of the Soxhlet type. Then the chloroform-treated raw material was dried and was exhaustively extracted with 70% ethanol. The ethanolic extracts were evaporated in vacuum to give a small residue. On standing in the refrigerator, substance (I) partially crystallized out. The deposit was separated off and the mother solution was deposited on a column of polyamide sorbent and was eluted successively with water and ethanol of various concentrations.

The fractions eluted by 15% ethanol contained substance (I) and those with 60% ethanol contained substance (II). Traces of (II) were also present in the chloroform extract. Substance (I), $C_{27}H_{30}O_6 \cdot 3H_2O$, mp 189-192°C, $[\alpha]_D^{20}$ −30° (c 0.51; ethanol), λ_{max} 363, 260 nm, was identified as quercetin 3-O-rutinoside (rutin) [2].

Substance (II), $C_{15}H_{10}O_7$, mp 310-313°C, was characterized as quercetin [2]. The rutin and quercetin were determined quantitatively by a spectrophotometric method after the preliminary separation of the flavonoids on chromatographic paper in the butan-1-ol—CH_3COOH—H_2O (4:1:5) system [2]. The amount of rutin was 6.5-6.7% and of quercetin 0.4-0.5%, calculated on the absolutely dry raw material. The high rutin content (about 7%) in the leaves of Dzhungarian willow permit us to recommend it as a source for the industrial production of rutin.

The phenolic glycosides were isolated by exhaustive extraction of the bark of the Dzhungarian willow with ethanol. The ethanolic extracts were evaporated in vacuum to a small residue, and this was diluted with water and purified with chloroform. The aqueous extract was treated with a 10% solution of basic lead acetate to precipitate tannin substances and flavonoids, these were filtered off, and the filtrate was freed from an excess of lead ions by hydrogen sulfide. Then it was extracted with ethyl acetate, and the extract was evaporated off. On standing in the cold, white crystals of the total phenolic glycosides deposited. The crystals were separated off, dissolved in a small amount of ethanol, deposited on a column of cellulose, and eluted with butan-1-ol—xylene—water (2:8:8), 25- to 30-ml fractions being collected [3].

Fractions 20-28 yielded a substance with the composition $C_{15}H_{20}O_7$, mp 173-175°C (water-saturated ethyl acetate), $[\alpha]_D^{20}$ −60° (c 1.47; water). The products of enzymatic hydrolysis with emulsin contained 4-hydroxycinnamyl alcohol and D-glucose. On the basis of the investigations performed, and also from an interpretation of the IR and UV spectra, the compound isolated was identified as 4-hydroxycinnamyl β-D-glucopyranoside (triandrin) [3].

Fractions 39-51 yielded a compound with the composition $C_{15}H_{18}O_7$, mp 198-201°C (water saturated ethyl acetate), $[\alpha]_D^{20}$ −60° (c 1.12; water). The phenolic glycoside isolated proved to be saligenin 2-O-β-D-glucopyranoside (salicin) [4]. The quantitative determination of the phenolic glycosides was performed by an improved gravimetric method [2]: the total amount was 3.5% calculated on the absolutely dry weight of the bark.

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A FLAVONOID FROM *Achillea cartilaginea*

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Among the flavone glycosides that we have isolated from the flower heads of *Achillea cartilaginea* [1], compound (VIII) with mp 221-224°C, $[\alpha]_D^{20}$ 138.6° (c 0.66; formamide) was erroneously identified as apigenin 7-O-β-D-glucopyranoside.

Acetylation of the glycoside gave, instead of the expected hexaacetate, a pentaacetate with the composition $C_{33}H_{32}O_{16}$, mp 200-203°C. Careful investigation of the products of acid hydrolysis (20% H_2SO_4, 6 h at 100°C) showed the presence of apigenin and glucuronic acid. The presence of a band at 1745 cm^{-1} in the IR spectrum of compound (VIII) and of three aliphatic acetoxy groups in the pentaacetate (NMR, Fig. 1) also confirms the presence of a uronic acid residue. Furthermore, in the NMR spectrum of the acetate there is the doublet (4.22 ppm, J = 9 Hz) of a proton at C-5" of a D-glucuronide and the signals of an ethoxycarbonyl group (triplet, 3 H at 1.2 ppm, and quartet, 2 H at 4.15 ppm).

Consequently, the carbohydrate moiety of compound (VIII) is ethyl D-glucuronate, the position of attachment of which at the 7-OH group of apigenin was shown previously from UV spectra.

In the NMR spectrum of the TMS ether of the glycoside, the two-proton quartet corresponding to the $-CH_2O$ group in the $-COOCH_2CH_3$ fragment fuses with the signals of the four protons of the glucuronic acid, forming a multiplet in the 3.5-4.15 ppm region with an intensity of 6 H. The signal of the anomeric proton (4.92 ppm, J = 6.5 Hz) corresponds to a β-bound D-glucopyranosiduronate. Thus, compound (VIII) has the structure of ethyl (apigenin 7-O-β-D-glucopyranosid)uronate.

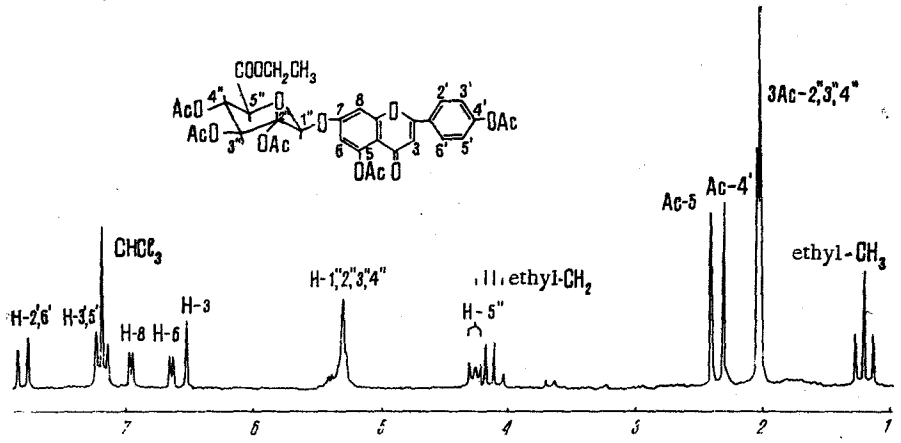

Fig. 1. NMR spectrum of the pentaacetate of ethyl (apigenin 7-glucosid)uronate in $CDCl_3$ (100 MHz, internal standard DMS).

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