by one additional secondary hydroxy group. The dehydrogenation of both alcohols (IV) and (VI) gave the one azulene (VII).

The multiplicity of the signal of the secondary hemihydroxyl methine proton in the spectrum of akichenol at 3.3 ppm (q, $J_1 = J_2 = 10$ Hz) shows that it interacts with only two other protons. This pattern can be observed only if this hydroxyl is present at C_2 or C_3. The resistance of akichenol to oxidation with periodic acid excludes the C_3 position.

Thus, it is most likely that akichenol (IV) has the structure of the triol corresponding to (I). When (I) was hydrolyzed with 1% ethanolic caustic potash in the cold for 2 h, we obtained a monoester (VIII) with the composition $C_{20}H_{32}O_4$, M^+ 336, the NMR spectrum of which showed an upfield shift of the sextet at 5.5 ppm (H-6) by 1.6 ppm with a simultaneous disappearance of the signals of the protons of p-hydroxybenzoic acid. It follows from this that the p-hydroxybenzoic residue is present at C_6 and the angelic acid residue at C_2. Consequently, akichenin has the most probable structure (I).

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CATECHIN-7-XYLOSIDE FROM *Spirea hypericifolia*

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As reported previously [1], in an investigation of the stems of S. hypericifolia we found two catechin glycosides. The present paper describes an investigation of a catechin xyloside.

The glycoside extracted from the raw material with methanol was separated from catechins and polyflavones by chromatography on Kapron using methanol–chloroform (9 : 1) as eluent. The separation of the flavan glycosides from one another was achieved by subsequent chromatography on silica gel (with ether and ethyl acetate as eluents).

The glycoside was isolated in the form of colorless needles with the composition $C_{20}H_{22}O_{10}$, mp 165-167°C, $[\alpha]_D^{20}$ −18.0° (c 3.89; acetone). The elementary analyses of the substance itself and of its derivatives corresponded to the calculated figures.

In the products of acid hydrolysis (+)-catechin and xylose were found. Acylation by acetic anhydride in pyridine yielded a heptaacetyl derivative $C_{34}H_{36}O_{17}$ in the form of colorless needles with mp 179-181°C $[\alpha]_D^{20}$ −75.0° (c 0.12; acetone), R_f 0.28 on TLC in benzene–acetone (9 : 1); NMR ($CDCl_3$) δ (ppm): 1.94 (1 alip Ac), 2.02 (3 alip Ac of a sugar), and 2.22 (3 ar Ac). Methylation with diazomethane at room temperature for 120 h gave a trimethyl derivative $C_{23}H_{28}O_{10}$ in the form of plates with mp 172-173°C, $[\alpha]_D^{20}$ −70.0° (c 0.66; methanol); R_f 0.44 in the benzene–acetone (9 : 1) system; NMR ($CDCl_3$), δ (ppm): 3.78 ($1CH_3O$), 3.89 ($2CH_3O$). The acetyl and methyl derivatives were purified on columns of silica gel–Chromaton (5 : 1) using mixtures of benzene and acetone (9 : 1 and 7 : 3) as eluents. A tetraacetyltrimethyl derivative of catechin xyloside was obtained with R_f 0.43 in the benzene–acetone (9 : 1) system; M^+ 632, which corresponds to the calculated molecular weight. The formation of a tri- and not a tetramethyl ether with diazomethane and the presence of the signal of an aliphatic acetyl group at δ 1.94 in the NMR spectrum showed that the sugar is attached to the phenolic hydroxyl.

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The position of the sugar in the catechin molecule was established by comparing the trimethyl ether of catechin obtained by the hydrolysis of the trimethyl ether of the glycoside by 5% sulfuric acid with various methyl ethers of (+)-catechin which we synthesized by literature methods [2, 3]. The melting point of 256-257°C and R_f 0.40 on TLC in the benzene–acetone (8 : 2) system correspond to the 3', 4', 5-trimethyl ether of (+)-catechin. The pyranose form of the ring and the β configuration of the anomeric center of the sugar were established by a Klyne analysis of molecular rotations, by enzymatic hydrolysis with emulsin, and by IR spectroscopy (890, 1045, 1075, 1090 cm^{-1}). In the NMR spectrum of the methyl derivative of the glycoside, the C_1–H signal of xylose at δ 4.88 ppm has J = 7 Hz.

Thus, the glycoside investigated is (+)-catechin 7-β-D-xylopyranoside. A similar compound has been isolated previously only from Ulmus americana [3].

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PHENOLIC COMPOUNDS OF Ononis arvensis. III

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We have previously reported [1] the isolation of a substance C from the roots of Ononis arvensis L. We now give the results of a determination of the structure of this compound. Substance C, with the composition $C_{22}H_{22}O_{10}$, mp 193-194°C (ethanol) $[\alpha]_D^{20}$ –158° (c 0.1; methanol), R_f 0.58 (3% HCOOH), has a pale violet fluorescence in UV light and when a chromatogram was treated with a mixture of ferric chloride and potassium ferrocyanide (1% aqeuous solution, equal volumes), it gave a deep blue coloration, which shows its phenolic nature [2]. The formation of an emerald green coloration with a 5% solution of gallic acid and a violet coloration with chromotropic acid indicated the presence of a methylenedioxy group in the substance under investigation [3, 4]. D-Glucose was identified in the products of acid, enzymatic, and alkaline hydrolysis. The aglycone could not be isolated from the hydrolyzate because of its lability. The acetate of this glycoside, with the composition $C_{30}H_{30}O_{14}$, obtained by a standard method [6], crystallized from methanol in the form of pale pink needles associated into druses with mp 183-184.5°C.

The UV spectrum of substance C has absorption maxima in the 285- and 310-nm regions (log ε 4.11 and 4.31), which is characteristic of isoflavanones [7]. No displacement of the absorption maxima was observed on the addition of ionizing and complex-forming reagents. The IR spectrum showed absorption bands at 3380 (OH), 2900 (CH_2, CH), 1621, 1597, and 1502 cm^{-1} (Ar) but there was no band characteristic for a C = O group.

The PMR spectrum of the trimethylsilyl ether in CCl_4 showed the signals (0 – TMS, δ scale) of five aromatic protons: 7.25 ppm (doublet, H-5 proton, J = 8.5 Hz), 6.58 ppm (quartet, H-6 proton, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 6.43 ppm (doublet, H-8 proton, J = 2.5 Hz), 6.55 ppm (singlet, H-2' proton), and 6.27 ppm (singlet, H-5' proton). A two-proton signal at 5.79 ppm corresponds to a methylenedioxy group in the 3',4' position. In addition, the following signals appeared: doublet of the H-4 proton (5.31 ppm, J = 6.5 Hz), multiplet of the H-3 proton (4.10 ppm), doublet of the aromatic proton of glucose at C_7 (4.73 ppm, J = 6.5 Hz), and the masked signal of the two protons at C_2 (3.66 ppm). The six protons of the glucose residue gave a complex, unresolved multiplet with its center at 3.4 ppm.

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