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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The PMR spectrum of the acetate of substance C in $CDCl_3$ (0 – TMS) has the following signals: 7.41 ppm (doublet of the H-5 proton, J = 8.5 Hz), 6.6 ppm (quartet of the H-6 proton, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 6.69 ppm (singlet of the H-2' proton), 6.58 ppm (doublet of the H-8 proton, J = 2.5 Hz), 6.40 ppm (singlet of the H-5 proton), 5.88 ppm (singlet of the 3',4'-methylenedioxy group), and 5.44 ppm (doublet of the H-4 proton, J = 2.5 Hz). A complex, unresolved multiplet of four sugar protons has its center at 5.19 ppm, and a two-proton signal of the methylene group of the glucose appears at 4.25 ppm. In the 3.35-4.19 ppm region there is a multiplet group of signals of the H-3, 2H-2, and H-5" signals of the carbohydrate residue, and at 2.05 ppm the signals of four acetyl groups of acetylated glucose.

Thus, on the basis of UV, IR, and PMR spectra substance C has been identified as 3',4'-methylenedioxypterocarpan 7-O-β-D-glucopyranoside or trifolirizin [5, 8]. This is the first time that this compound has been isolated from the genus Ononis.

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THE STRUCTURE OF TEFERIDIN – A NEW ESTER FROM THE FRUIT OF Ferula tenuisecta

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Continuing a study of the esters of plants of the genus Ferula [1-4] from the fruit of Ferula tenuisecta Eug. Kor., we have isolated a new ester with the composition $C_{22}H_{30}O_3$, M^+ 342, $[\alpha]_D$ +37.5° (c 1.0; chloroform), which we have called teferidin. The substance is readily soluble in all organic solvents and insoluble in water.

The UV spectrum of teferidin shows a maximum at 231 nm (log ε 3.58) and the IR spectrum has absorption bands at (cm^{-1}) 3400-3600 (hydroxy group), 1725 (ester carbonyl), and 1620, 1580, and 1520 (aromatic nucleus).

When the substance was hydrolyzed by heating with 5% aqueous methanolic caustic potash, the neutral fraction yielded an alcohol with the composition $C_{15}H_{26}O_2$, mp 91-92°C, identical with ferutinol [2], and the acid fraction of the hydrolyzate yielded benzoic acid with mp 119-120°C.

The hydrolysis products of teferidin were identified by mixed melting points and IR spectroscopy.

Thus, teferidin is an ester of ferutinol and benzoic acid. The position of the acid residue was established by the chemical shift and multiplicity of the signal of the hemiacyl proton in the NMR spectrum of teferidin, which appeared in the form of a sextet ($J_1 = J_2 = 10$ Hz, $J_3 = 4$ Hz) at 5.17 ppm. It follows from this that the benzoic acid residue in the teferidin molecule, as in ferutin and ferutinin [1, 2], ferutidin [3], and terefin [4], is located on the secondary hydroxy group.

In addition to teferidin, we also isolated ferutin and ferutinin from the fruit, these being identified by mixed melting points [1, 2].

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