PHENOLIC COMPOUNDS OF Ononis arvensis

THE STRUCTURE OF ONOGENIN

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Continuing a study of the roots of Ononis arvensis L., we have isolated a substance $C_{17}H_{14}O_6$ with mp 213-214° C (from ethanol), mol. wt. 314 (mass spectrometry), R_f 0.76, 0.69 (chloroform–formamide and 40% acetic acid systems), which we have called onogenin.

Onogenin is soluble in methanol, ethanol, chloroform, acetone, and alkalis and is insoluble in water and acid. When chromatograms were treated with a mixture of ferric chloride and potassium ferrocyanide (1% aqueous solutions, in equal volumes), the substance formed a deep blue coloration, which shows its phenolic nature [1].

In filtered UV light it gave a yellow-green fluorescence disappearing when the chromatogram was treated with a 10% ethanolic solution of alkali. The results of analyses of the products of acid and alkaline hydrolysis showed the aglycone nature of onogenin.

In UV light, absorption maxima were found at 308 and 278 nm (log ε 4.19, 4.15), which is characteristic for isoflavanones in which ring B is not conjugated with the pyrone carbonyl group or this conjugation is weak [2]. A bathochromic shift of the maxima in the presence of sodium acetate by 8 mm and in the presence of alkali by 32 nm showed that the hydroxy group is located in the C_7 position [3].

The IR spectrum of onogenin (Fig. 1) showed absorption bands in the following regions: 3320 cm^{-1} (phenolic hydroxyl), 2950, 2900, 2845 cm^{-1} ($-CH_2$, $-OCH_3$, C–H), 1665 cm^{-1} (C=O of an isoflavanone), 1590, 1509, and 1489 cm^{-1} (skeletal vibrations of aromatic rings A and B), and 1118 and 1038 cm^{-1} ($-OCH_3$). A strong band at 931 cm^{-1} and one of medium intensity at 727 cm^{-1} are characteristic of a methylenedioxy grouping of an aromatic system [4]. Positive reactions with a 5% solution of gallic acid in the presence of concentrated sulfuric acid and with chromotropic acid in 72% sulfuric acid showed the presence of a methylenedioxy group [5, 6].

The PMR spectrum of the trimethylsilylether of onogenin (Fig. 2) contained the signals of five aromatic protons: a doublet from the H-5 proton at 7.74 ppm, J = 8 Hz; a quartet from the H-6 proton at 6.40 ppm; J_1 = 8 Hz, J_2 = 2 Hz; a doublet from a H-8 proton at 6.26 ppm, J = 2 Hz; and singlets at 7.26 and 7.43 ppm corresponding to the H-2' and H-5' protons. The H-6 quartet is partially masked by the singlets of

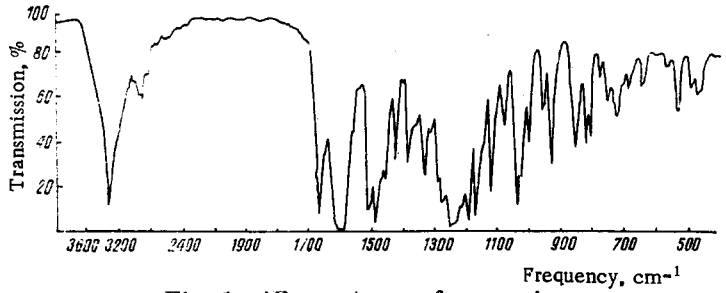

Fig. 1. IR spectrum of onogenin.

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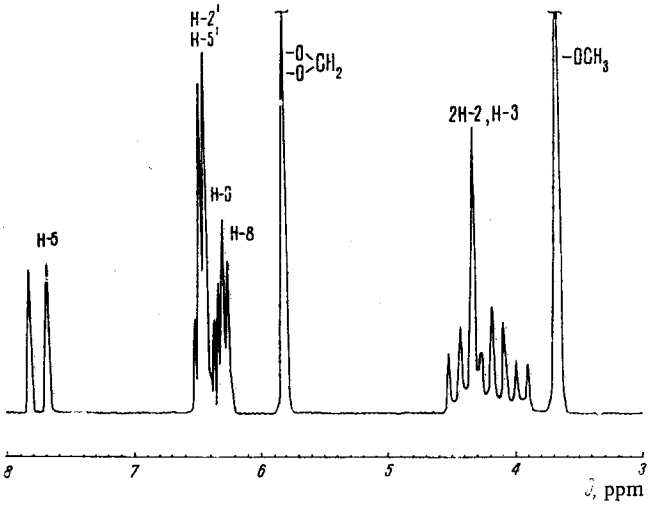


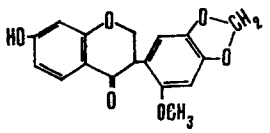
Fig. 2. NMR spectrum of the trimethylsilyl ether of onogenin.

the protons of the B ring. The singlet nature of the signals is due to a distance between them and was shown by the addition of acetone to a solution of onogenin acetate in $CDCl_3$, when they overlapped and gave a single line. This confirms that the two protons of ring B are present in the para position.

A two-proton singlet at 5.81 ppm is due to the 3',4'-methylene dioxy group of the lateral ring [7]. The presence of a signal of a methoxy group at 3.78 ppm made it possible to assume that this group was present in position 6'. The signals of the 2H-2 and H-3 protons, overlapping, form a complex three-proton multiplet with its center at 4.32 ppm in which it does not appear possible to assign the individual lines.

A further confirmation of the assignment given above was obtained by an analysis of the PMR spectrum of onogenin acetate. The spectrum contained the signal of one acetyl group at 2.29 ppm, which shows the presence of only one hydroxy group in the initial compound. The nature of the signals of the aromatic protons of ring A show that the hydroxy group is present in position C_7. This is also shown by the stronger shift of the signals of the protons of ring A of the acetate downfield as compared with the signals of the protons of ring B. In addition, the spectrum contains the following signals: a doublet from the H-5 proton at 7.98 ppm, J = 8 Hz; a quartet from the H-6 proton at 6.77 ppm, J_1 = 8 Hz, J_2 = 2 Hz; a doublet from the H-8 proton at 6.76 ppm, J = 2 Hz; and two singlets at 7.58 and 7.54 ppm due to the H-2' and H-5' protons. Singlets at 5.88 and 3.70 ppm correspond to the 3', 4'-methylenedioxy and 6'-methoxy groups. The 2H-2 and H-3 protons form a complex multiplet with its center at 4.48 ppm. These facts are in complete agreement with the assignment of the signals in the PMR spectrum for the trimethylsilyl ether of onogenin.

Thus, on the basis of the above facts the structure of 7-hydroxy-6'-methoxy-3',4'-methylenedioxyisoflavanone is proposed for onogenin:



EXPERIMENTAL METHOD

For analysis, the substances were dried over P_2O_5 in vacuum at 100-115° C for 4 h. The specific rotations were determined on an SPU-M spectropolarimeter. The results of the measurements showed that the substance is optically inactive.

The UV spectra were taken on an SF-4A spectrophotometer, the IR spectra on a UR-10 instrument, and the PMR spectra on a Hitachi–Perkin–Elmer R-20 A instrument at a working frequency of 60 MHz (δ scale). The measurements were performed at 34.5° C, the solvent was carbon tetrachloride or, for the acetate, $CDCl_3$, and tetramethylsilane was used as internal standard. The TMS ether was obtained as described by Mabry et al. [7].

The mass spectra were determined on an MKh-1303 instrument at 80° C with an ionizing voltage of 70 V using an inlet system providing for the introduction of the sample into the ion source.

The acetate was obtained by a known method [8], in the form of light pink crystals with mp 156-158° C (from ethanol).

SUMMARY

From the roots of Ononis arvensis L. a new isoflavone has been isolated with mp 213-214° C which has been called onogenin. On the basis of the results of a study of its UV, IR, NMR, and mass spectra, the structure of 7-hydroxy-6-methoxy-3',4'-methylenedioxyisoflavanone is proposed for onogenin.

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