FLAVONOID GLUCURONIDES FROM Cirsium arvense

V. L. Shelyuto, V. I. Glyzin, and N. T. Bubon

UDC 547.972

From the flowers of Cirsium arvense L. (Canada thistle), in addition to the apigenin, luteolin, 3-O-methylkaempferol, and cosmosiin obtained previously, we have isolated two flavonoid glucuronides, A and B.

Substance A, $C_{21}H_{18}O_{11} \cdot H_2O$, melts above 300°C, $[\alpha]_D - 119°$ (c 0.6; formamide), λ_{max} 270, 330 nm. The acid hydrolysis of substance A with conc. sulfuric acid and with the enzyme preparation "Avamorin" gave an aglycone $C_{15}H_{10}O_5$ with mp 349-351°C, identified as apigenin, and glucuronic acid, identified by paper chromatography.

In order to establish the position of attachment of the glucuronic acid, the UV spectrum of substance A was taken with ionizing and complex-forming reagents. In the presence of sodium methoxide, a bathochromic shift of the maximum of the long-wave band by 58 nm was observed (free hydroxy group in position 4'). The presence of a free hydroxy group in position 5 was shown by a bathochromic shift of the maximum of the long-wave band by 62 nm with zirconium nitrate. Thus, the glucuronic acid residue can be only in position 7.

The NMR spectrum of silylated substance A (Fig. 1) showed the following signals: doublet at 7.72 ppm (2 H) (J = 8.5 Hz) – 2',6'; doublet at 6.8 ppm (2 H) (J = 8.5 Hz) – 3',5'; two doublets each with an intensity of one proton unit at 6.44 and 6.28 ppm (J = 2.5 Hz) corresponding to protons in positions 8 and 6; a singlet at 6.42 ppm with an intensity of one proton unit due to a proton in position 3; and a doublet at 5.00 ppm with an intensity of one proton unit (J = 7 Hz) corresponding to the anomeric proton of the glucuronic acid. The spin-spin coupling constant shows the β configuration of the link of the glucuronic acid with the aglyone. The remaining protons of the silylated glucuronic acid are represented by signals in the 3.4-3.9 ppm region (4H). The pyranose form of the glucuronic acid ring was established by comparing the molecular rotations of substance A and of known flavonoid glucuronides.

Thus, substance A is apigenin 7-β-D-glucopyranosiduronic acid.

Substance B, $C_{22}H_{20}O_{11} \cdot H_2O$, mp 245-247°C, $[\alpha]_D - 107.1°$ (c 0.6; formamide), λ_{max} 269, 335 nm. The hydrolysis of substance B gave the aglycone acacetin, $C_{16}H_{12}O_5$, with mp 261-263°C, identified by its UV, IR

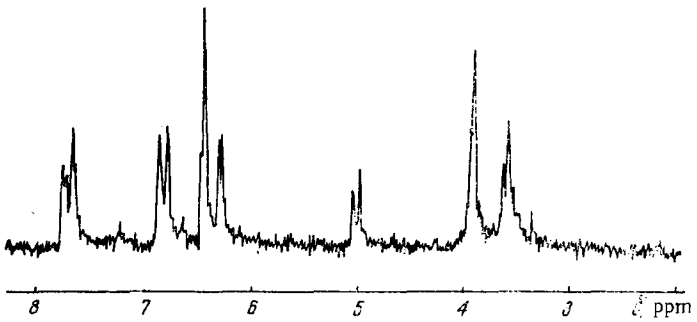

Fig. 1. NMR spectrum of silylated apigenin 7-β-D-glucosiduronic acid.

Vitebsk Medical Institute. All-Union Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 240-241, March-April, 1972. Original article submitted September 23, 1971.

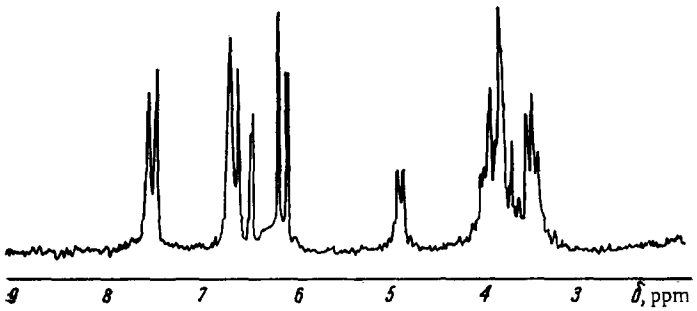

Fig. 2. NMR spectrum of silylated acacetin 7-glucosiduronic acid.

and NMR spectra and by direct comparison with an authentic sample. Glucuronic acid was identified in a hydrolysate by paper chromatography. The position of attachment of the glucuronic acid was shown by analogy with substance A.

In the NMR spectrum of silylated substance B (Fig. 2), a doublet at 7.68 ppm (2H) (J = 8.5 Hz) corresponds to the 2',6' protons; a doublet at 6.80 (2H) (J = 8.5 Hz) to the 3',5' protons; two doublets of one proton unit each with J = 2.5 Hz at 6.60 and 6.24 ppm are due to the H-8 and H-6 protons; a singlet at 6.32 ppm is characteristic of the H-3 proton; and a doublet at 4.94 ppm (J = 7 Hz) with an intensity of one proton unit relates to the anomeric proton of the β-glucuronic acid. Four protons of the glucuronic acid are represented by signals in the 3.3-3.9 ppm region. The pyranose form of the glucuronic acid ring was established by analogy with substance A.

The results obtained identify substance B as acacetin 7-β-D-glucopyranosiduronic acid.