FLAVONOIDS OF THE GENUS Crataegus

THE STRUCTURE OF BIOQUERCETIN

V. I. Bykov, V. I. Glyzin,
and A. I. Ban'kovskii

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Continuing a study of the flavonoid composition of plants of the genus Crataegus (hawthorne), from the leaves of C. pinnatifida Bge. we have isolated a compound with the composition $C_{27}H_{30}O_{16} \cdot {}^1/_2H_2O$, mp 194-199°C, $[\alpha]_D^{20} -34.8°$, λ_{max} 362, 258 nm.

The IR spectrum of the substance shows absorption bands due to the stretching vibrations of a hydroxy group (3350 cm^{-1}, broadened peak), of a carbonyl group (1655 cm^{-1}), and of conjugated double bonds (1605, 1585, 1504 cm^{-1}). The IR spectra taken with the use of diagnostic reagents shows the presence of free hydroxy groups in it at C_5, C_7, C_3', and C_4'.

The acid hydrolysis of the flavonoid gave quercetin $C_{15}H_{10}O_7$, mp 308-313°C, λ_{max} 375, 256 nm. As sugar components, galactose and rhamnose were identified by paper chromatography in the benzene–butan-1-ol–pyridine–water (1 : 5 : 3 : 3) system [1].

The spectral characteristics of the glycoside and its aglycone show that the carbohydrate moiety is present in the form of a biose in position 3.

The constants of the substance and the products of its hydrolysis correspond to bioquercetin, for which the structure of quercetin 3-O-[β-L-rhamnopyranosyl-(1 → 6)-β-D-galactofuranoside] has been suggested [2].

In the NMR spectrum of the silylated glycoside there are the following signals (ppm): quartet with its center at 7.65, 1H, J = 2.5 Hz, and J' = 9 Hz (H-6'); doublet at 7.22, 1H, J = 2.5 Hz (H-2'); doublet at 6.75, 1H, J = 9 Hz (H-5'), doublet at 6.37 ppm, 1H, J = 2.5 Hz (H-8); doublet at 6.06, 1H, J = 2.5 Hz (H-6); doublet at 5.56, 1H, J = 8 Hz (proton of the anomeric center of β-galactose in position 3 of the flavonol); doublet at 4.28 ppm, 1H, J = 2 Hz (proton of the anomeric center of α-rhamnose attached to the galactose in position 6); multiplet in the 3.20-3.80 ppm region, 1OH (protons of the biose) [3].

Exhaustive methylation of the flavonoid with subsequent methanolysis of the ether formed led to the methyl glycosides of 2,3,4-tri-O-methyl-L-rhamnose and 2,3,4-tri-O-methyl-D-galactose, which were identified by gas–liquid chromatography from their relative retention times [4].

The results obtained show that in the compound isolated the galactose has the β configuration of the glycosidic center and a pyranose ring and the rhamnose the α configuration and a pyranose ring. Thus, in our opinion, bioquercetin has the structure quercetin 3-O-[α-L-rhamnopyranosyl-(6 → 1)-β-D-galactopyranoside].

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