FLAVONOIDS AND CHLOROGENIC ACID FROM Sorbus tianschanica. II.

G. G. Zapesochnaya, R. Kh. Aitbaeva,
and A. I. Ban'kovskii

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Continuing a chemical study of Tien-Shan mountain ash [1], we have isolated – in addition to hyperin (I) – hirsutrin (II), $C_{21}H_{20}O_{12}$, mp 228-230°C, $[\alpha]_D^{20}$ −32°C (formamide), and chlorogenic acid (III), $C_{16}H_{18}O_9$, mp 205-207°C, $[\alpha]_D^{20}$ −37.7° (methanol). The fruit contains mainly substances (I) and (III) and the leaves and flowers mainly (II).

Compound (II) was identified as hirsutrin (quercetin 3-O-β-D-glucopyranoside) [2] on the basis of the results of acid hydrolysis (quercetin and D-glucose, 1 : 1), methylation and subsequent hydrolysis (3-hydroxy-3',4',5,7-tetramethoxyflavone, mp 194°C), and the acetylation of the glycoside (octaacetate, $C_{37}H_{36}O_{20}$, mp 166-167°C. Literature data: mp of hirsutrin octaacetate 156-157°C and that of quercitrin 168-170°C [2], 179-180°C [3]).

The structures of the compounds isolated were also confirmed by their NMR spectra, taken after silylation in carbon tetrachloride. In 3-O-glucosides and galactosides, the signal of the C-1'' proton is located near 5.8 ppm. The C-1'' proton of a β-linked sugar undergoes diaxial splitting with the C-2'' proton and appears in the form of a doublet with a coupling constant of about 7 Hz [4], as has been found for compounds (I) and (II).

In the NMR spectrum of compound (III) after silylation (solution in CCl_4) the signals of the protons of caffeic acid were observed: multiplet at 3 H with its center at 6.85 ppm (2',5', and 6' aromatic protons) and two doublets of vinyl protons present in the trans position at 6.02 and 7.40 ppm (J 16 Hz).

Since silylation may cause a change in the conformation of quinic acid [5], the nature of the aliphatic protons of compound (III) was studied by recording the NMR spectrum in deuteropyridine. The H-4 proton gave a double doublet at 4.21 ppm (J 8.5 Hz, J_1 3 Hz), H-3 a quartet at 4.67 ppm (J 3 Hz), and H-5 a triplet of doublets at 6.08 ppm with a width of 23 Hz (J 9 Hz, J_1 5 Hz); a multiplet at 2.42-2.92 ppm with an intensity of 4 H corresponded to the protons at C-2 and C-6 of quinic acid. The results obtained correspond to those given in the literature for chlorogenic acid [5, 6]. In the present paper, as in the cited one [5], quinic acid (IV) is numbered according to published rules [7], and therefore chlorogenic acid is not 3- but 5-O-caffeylquinic acid.

In the NMR spectrum (solution in $CDCl_3$) of the pentaacetate there are the signals of five acetyl groups: singlets at (ppm) 2.30 (6 H), 2.01 (3 H), 2.11 (3 H), and 2.15 (3 H). The spectrum also exhibits a well-defined double doublet of an H-4 axial proton (δ 5.14 ppm, J 10 Hz, J_1 4 Hz), which shows the retention of the conformation of quinic acid, since in the formation of a quinide inversion takes place with the production of a conformation (V) in which the COOH and 5-OH groups are axial and the proton at C-4 is equatorial [6].

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