FLAVONOIDS OF *Gnaphalium sylvaticum*

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We have previously isolated luteolin and quercetin from *Gnaphalium sylvaticum* L. [1]. On further separation of the combined flavonoids on a column of polyamide sorbent, we have isolated substances (I) and (II) from the ethereal fractions and (III) and (IV) from ethyl acetate fractions. A positive cyanidin reaction of the substances and the results of UV spectroscopy show the flavonoid nature of the compounds isolated.

Substance (I), with the composition $C_{17}H_{14}O_7$, mp 287-289°C, λ_{max} 245, 272, 352 nm. The UV spectra of the substance in the presence of sodium ethoxide, aluminum chloride, and sodium acetate showed that there were free hydroxy groups in positions 4', 5, and 7.

The NMR spectrum of the substance had the signals of H-6 and H-8 protons in the form of two doublets at 6.54 and 6.24 ppm, J = 2.5 Hz (1H each); that of H-3 as a singlet at 6.70 ppm (1H); and a singlet at 7.36 ppm (2H) due to the signals of the H-2',6' protons. Thus, ring B has three substituents in positions 3', 4', and 5', one of them being a hydroxy group in the 4' position and the other two being methoxy groups in the 3' and 5' positions.

The mass spectrum of the substances, with M^+ 330, and m/e 152, 181, and 178 confirmed the inferences from the UV and NMR spectra.

According to the results obtained, substance (I) has the structure of 4',5,7-trihydroxy-3',5'-dimethoxyflavone and is identical with tricin [2].

Substance (II), with the composition $C_{15}H_{10}O_5$, mp 345-350°C, λ_{max} 268, 336 nm was identified as apigenin on the basis of UV, IR, NMR, and mass spectroscopy [3].

Substance (III), with the composition $C_{21}H_{20}O_{12}\cdot H_2O$, mp 212-215°C, λ_{max} 255, 362 nm, $[\alpha]_D^{20}$ −40° (c 0.13; methanol).

Hydrolysis of the substance yielded an aglycone that was identified as quercetin and glucose, which was identified by paper chromatography.

The NMR spectrum of the substance had the following signals: m 7.50 ppm (2H), H-2',6'; d 6.86 ppm, J = 8 Hz, H-5'; d 6.42 ppm, J = 2.5 Hz (1H), H-8; d 6.14 ppm, J = 2.5 Hz (1H), H-6; and d 5.84 ppm, J = 7 Hz — the signal of the glycosidic center of the β-glucose attached at position 3; signals in the 3.2-3.8 ppm range correspond to the six glucose protons.

The results of UV spectroscopy showed the presence of free hydroxy groups in positions 3', 4', 5, and 7.

On the basis of the facts given, it may be concluded that substance (III) has the structure of quercetin 3-O-β-D-glucopyranoside and is identical with isoquercitrin [4].

Substance (IV), with the composition $C_{21}H_{20}O_{12}$, mp 243-245°C, λ_{max} 260, 270, and 369 nm. Acid hydrolysis gave an aglycone, which was identified as quercetin, and glucose.

The results of UV spectroscopy showed the presence of free hydroxy groups in positions 3, 3', 4', and 5, and the substitution of the hydroxy group in position 7 by glucose, as was confirmed by the NMR spectrum of the substance.

The results of UV, IR, and NMR spectroscopy permit the conclusion that the substance we isolated has the structure of 3,3',4',5-pentahydroxyflavone 7-O-β-D-glucopyranoside and is identical with quercimeritrin [5].

This is the first time that any of the compounds mentioned have been isolated from *Gnaphalium sylvaticum* L.

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SONCHOSIDE — A NEW FLAVONOID GLYCOSIDE FROM *Sonchus arvensis*

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We have previously reported the isolation from the flowers of *Sonchus arvensis* (field sowthistle) of luteolin, cynaroside, isocynaroside, quercetin, quercimetrin, chrysoeriol, and isorhamnetin, and an isorhamnetin 3-glycoside [1-3]. Continuing our investigations of the flowers of this plant, we have isolated a flavonoid glycoside with the composition $C_{21}H_{20}O_{12}$, mp 240-243°C, $[\alpha]_D^{20}$ −59.6° (c 0.5; formamide), λ_{max} 266, 380 nm.

Hydrolysis of the glycoside yielded glucose, identified by paper chromatography, and an aglycone with the composition $C_{15}H_{10}O_7$, M^+ 302.

In the region of the signals of aromatic protons in the NMR spectra of the substance there was a singlet at 7.39 ppm, 1H, a singlet at 7.18 ppm, 1H, two doublets at 6.82 and 6.52 ppm, 1H each, J = 2.5 Hz, and a singlet at 6.62 ppm, 1 H. On the basis of the results of an analysis of these signals, it may be concluded that in the ring A of the flavonoid there are substituents in positions 5 and 7.

The 6.62 ppm singlet is due to a proton in position 3. Consequently, this compound belongs to the group of flavonoids in ring B of which there are three substituents, and their positions can only be 3', 4', and 6'. The substituents in positions 3', 4', 5, 6', and 7 are hydroxy groups, as follows from the absence of the signals of protons of other possible substituents. The mass spectrum of the aglycone, with a molecular weight M^+ 302, corresponds to the spectrum of hieracin, for which the structure of 3',4',5,6',7-pentahydroxyflavone has been proposed previously. We first isolated this compound from the flowers of mouse-ear hawkweed [4]. The carbohydrate component of the glycoside is present in position 7, as was established by UV spectroscopy. The glucose had the β configuration of the glycosidic center (doublet at 4.84 ppm, J = 7 Hz, in the NMR spectrum, and the ring is in the pyranose form.

Thus, the glycoside isolated from the flowers of the field sowthistle has the structure of 7-β-D-glucopyranosyloxy-3',4',5,6'-tetrahydroxyflavone.

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