CHRYSOSPLIN—A NEW FLAVONOID FROM CHRYSOSPLENIUM PSEUDO-FAURIERI

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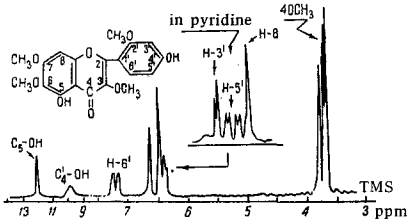
Chrysosplenium pseudo-faurieri Hara (Ch. trachyspermum Maxim.) (family Saxifragaceae) [1, 2] is an endemic plant growing in southern Primorye in the basin of the middle course of the Amur. The chemical composition of the plant has not been studied previously. A number of highly-methylated flavonols and their glycosides has been isolated from related species growing in Japan and China [3–6].

We have established that the herb contains a complex of flavonoids readily soluble in ethanol, ether, chloroform, and benzene and very sparingly soluble in water. By chromatography on a column of polyamide we have obtained a yellow crystalline substance $C_{19}H_{18}O_8$, mp 191–193° C, R_f 0.67 (15% acetic acid) giving the characteristic reactions for flavones. It contained four methoxyl and two hydroxyl groups (diacetate with mp 182–183° C). Consequently, of the eight oxygen atoms, two are present in a γ-pyrone ring, four in the form of methoxyl groups, and two in the form of hydroxyl groups. The mass spectrum of the flavone has the peak of the molecular ion M^+ 374, and four groups of peaks with m/e 359, 357; 343, 339; 331, 325; 313.

IR spectrum: cm^{-1}: 3350–3450, 1090, 1067 (hydroxyl groups), 2955, 2840 (CH_3O groups), 1650 (C=O of a flavone), and 1585, 1560, 1490 (aromatic nucleus).

UV spectrum, λ_{max} in ethanol: 237, 256, 335 mμ (log ε 4.24, 4.26, 4.14); + $AlCl_3$: 270, 350 mμ; + $ZrOCl_2$: 350 mμ; + $ZrOCl_2$ + citric acid: 333 mμ; + sodium ethoxide: 267, 380 mμ; + NaAc: 256, 335 mμ; + H_3BO_3: 256, 335 mμ. Thus, the UV spectra taken in the presence of ionizing and complex-forming reagents show the positions of the hydroxyl groups at carbon atoms 5 and 4'.



NMR spectrum of chrysosplin.

In the NMR spectrum (100 MHz, solution in DMSO) (figure) there are two signals with δ 12.50 and 9.91 ppm in the weak-field region due to the protons of the OH groups in positions 5 and 4', respectively [7, 8], and four singlets with δ 3.86, 3.76, 3.73, and 3.71 ppm (3H each) due to the protons of the four methoxyl groups. In the region of aromatic protons, four signals appear: two doublets with δ 7.21 ppm, J = 9.5 Hz, and δ 6.46 ppm, J = 9.5 Hz, due to the H-6' and H-5' protons, and two singlets with δ 6.65 ppm (H-3') and 6.51 ppm, which is fused with a doublet at 6.46 ppm (H-8). When the spectrum was recorded in pyridine solution, the doublet from H-6' partially fused with the signal of the solvent, and in the region of the other signals clear resolution was observed—a quadruplet at 6.53 ppm with J_1 = 9 Hz and J_2 = 1.8 Hz, a doublet at δ 6.66 ppm with J = 1.8 Hz, and a sharp singlet at 6.37 ppm caused by the H-5', H-3', and H-8 protons, respectively [9].

The demethylation of the flavone with HI and subsequent alkaline fusion yielded β-resorcylic acid, which was identified by paper chromatography.

It follows from what has been said above that the pigment isolated, which we have called "chrysosplin" is a new flavone containing a resorcyl nucleus (see figure): 5, 2'-dihydroxy-3, 6, 7, 2'-tetramethosyflavone.

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