FLAVONOIDS OF Atraphaxis pyrifolia. III

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We have previously [1] reported the isolation from the leaves of Atraphaxis pyrifolia of a flavonoid glycoside for which the structure of 7-methylgossypetin 3-O-α-L-rhamnopyranoside was proposed. In the present communication we correct the structure of this glycoside [it is denoted as glycoside (I)]. By chromatography on silica gel we isolated a glycoside (II) [solvent systems for chromatography: 1) BAW (4:1:5); 2) 15% CH_3COOH (FN-4 paper); and 3) ethyl acetate–chloroform (1:1) (TLC on "Silufol")], the acid hydrolysis of which yielded aglycone (II) and rhamnose, which was identified by chromatography with a marker. For glycoside (II) λ_{max} (nm): 260 (sh.), 274, 334, 362 (low int.) – ethanol; 259 (sh.), 334, 364 (low int.) – sodium acetate; 264, 380 – sodium acetate and boric acid; 274, 404 – zirconyl hydrochloride; the aglycone (II) – 272, 278 (sh.), 346, 384; 266, 396 – boric acid and sodium acetate; 272, 404 – zirconyl hydrochloride. Both substances gave a positive gossypetin reaction.

The physicochemical properties of the flavonoids of A. pyrifolia are given below.

Compound	Composition	mp, °C	$[\alpha]_D$	Rf_1	Rf_2	Rf_3
Glycoside (I)	$C_{24}H_{24}O_{13}$	156-158	−125.0	0.80	0.77	–
Aglycone (I)	$C_{18}H_{14}O_9$	270-272	–	0.82	0.10	–
Pentaacetate of aglycone (I)	$C_{26}H_{22}O_{13}$	224-225	–	–	–	0.67
Heptaacetate of glycoside (I)	$C_{36}H_{36}O_{19}$	140-142	−106.9	–	–	0.66
Glycoside (II)	$C_{22}H_{22}O_{12}$	183-185	−109.6	0.60	0.61	–
Aglycone (II)	$C_{16}H_{12}O_8$	315-317	–	0.53	–	–
Heptaacetate of glycoside (II)	$C_{36}H_{36}O_{19}$	140-142	−110.0	–	–	0.65
Pentaacetate of aglycone (II)	$C_{26}H_{22}O_{13}$	223-225	–	–	–	0.66

The results of the spectroscopic examination of glycoside (II) and its aglycone with diagnostic reagents showed that, as in the case of glycoside (I), the rhamnose was attached at position 3. The acetylation of glycoside (II) yielded a heptaacetate similar to the full acetate of glycoside (I). The acetates of the aglycones were also similar. In the IR spectrum of the glycoside (I) and its aglycone there is an absorption band at 1735 cm^{-1} which is characteristic for an ester grouping. It is absent from the spectrum of glycoside (II) and its aglycone.

The mild alkaline saponification of glycoside (I) gave a compound coinciding in its physicochemical constants and IR spectrum with glycoside (II), and acetic acid was detected chromatographically [2]. When glycoside (I) and its aglycone were subjected to prolonged boiling with hydrochloric acid–ethanol (1:1), an aglycone similar in its properties and chromatographic behavior to aglycone (II) were isolated.

The NMR spectra (for the glycosides we used the trimethylsilyl ethers in CCl_4, and the spectra of the aglycones were taken in pyridine) of glycoside (I) and its aglycone, in contrast to glycoside (II) and its aglycone, a signal with an intensity of three proton units was observed the position of which at δ 2.30 ppm shows that the acetyl group is attached to one of the aromatic hydroxyls. It follows from the UV spectra that the 3'-, 4'-, and

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5'-OH groups are free and the 7-OH group is substituted by a methyl, and the only possible position of substitution of an acetyl group is position 8.

On the basis of the facts obtained, we correct the structure of glycoside isolated previously and propose for glycoside (I) the structure of 8-acetylmethylgossypetin 3-O-α-L-rhamnopyranoside, for its aglycone 8-acetyl-7-methylgossypetin, and for glycoside (II) 7-methylgossypetin 3-O-α-L-rhamnopyranoside. They are new natural compounds and we propose to call them pyrifolin, pyrifolidin, and pyrifolinin, respectively. It must be mentioned that the aglycone 7-methylgossypetin which we obtained by the acid hydrolysis of glycoside (II) has a different melting point from the 7-methylgossypetin isolated from the flowers of Lothus corniculatus [3, 4].

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THE FLAVONOIDS OF Hieracium umbellatum

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We collected the plant Hieracium umbellatum L. (narrowleaf hawkweed) in the stage of full flowering in the environs of Vitebsk.

To isolate individual flavonoids, the epigeal part was extracted with ethanol in the boiling-water bath. The combined extracts were concentrated under vacuum to small volume, the residue was treated with carbon tetrachloride, and chromatography was carried out on a column of polyamide sorbent. Elution of the column with a mixture of ethanol and chloroform gave apigenin, luteolin, and a substance (III) with mp 266-268°C, $[\alpha]_D$ −54.7° (c 0.6; formamide), λ_{max} 255, 268, 350 nm. The product of the acid hydrolysis of (III) was an aglycone with mp 328-330°C giving an acetate with mp 224-226°C. A mixture of the aglycone of substance (III) with luteolin gave no depression of the melting point. The acid mother liquor was found by paper chromatography to contain glucose. On the basis of the results of UV, IR, and NMR spectroscopy it may be considered that the compound isolated was luteolin 7-β-D-glucopyranoside.

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