FLAVONOIDS OF Rhodiola algida

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A methanolic extract of the roots of Rhodiola algida (Ledeb.) Fisch. et Mey., family Crassulaceae, collected in the flowering phase of the plant at a height of 2000 m in the Gorno-Altai Autonomous Oblast (Bashchelykskii range), was chromatographed on polyamide in a gradient chloroform–methanol system. Flavonol glycosides (I-VI) were isolated (Table 1).

On acid hydrolysis, all the glycosides gave the same aglycone with the composition $C_{15}H_{10}O_7$, mp 278-280°C, mol. wt. 302 (mass spectrometry), λ_{max}^{MeOH} 226, 278, 330, 385 nm (the substance decomposed on the addition of all the diagnostic reagents); the reaction with p-benzoquinone showed the presence of a 5,8-dihydroxy grouping in the aglycone (gossypetone test). In the NMR spectrum of the TMS ether of the aglycone in CCl_4 (Varian HA-100D, 100 MHz, internal standard HMDS) there were signals of a 3,4',5,7,8-substituted flavone: two 2-proton doublets with J = 9 Hz at δ = 8.0 (H–2',6') and 6.76 ppm (H–3',5') and a singlet at 6.06 ppm (H–6).

The pentaacetate of the aglycone was obtained with the composition $C_{25}H_{20}O_{12}$, mp 185-186°C, the NMR spectrum of which (solution in $CDCl_3$) showed the signals of five acetoxy groups, while the signals of the aromatic protons were displaced: 6.9 ppm (H–6), 7.18 ppm (H–3',5'), and 7.7 ppm (H–2',6').

Thus, the aglycone was identified as 3,4',5,7,8-pentahydroxyflavone (herbacetin).

The carbohydrate moieties in (I) and (II) were identified as L-arabinose, in (III) and (IV) as D-xylose, and in (V) as glucuronic acid. Compound (VI) contained two sugars, one of which was according to preliminary results, glucuronic acid.

The NMR spectra of the glycosides taken in DMSO had a signal at 12.30 ppm of a free 5-OH group.

The glycosidation of compounds (I-V) apparently took place at position 4' of the aglycone, since the UV spectra of all the glycosides were identical (λ_{max}^{MeOH} 272, 327, 374 nm), and they contained free hydroxy groups at C_7 (NaOAc 282 nm) and C_3 ($AlCl_3$/HCl 436 nm). The stability to the action of NaOMe (282, 329,

TABLE 1. Physicochemical Constants of the Flavonoids

Compound	Composition	mp, °C (Koffler)	$[\alpha]_D^{20}$, deg. (in methanol)	IR spectrum, $\nu_{C=O}$, cm^{-1}	R_f*		
					PC 1	PC 2	TLC 3
Rhodalgin (I)	$C_{20}H_{18}O_{11}$	239–240	+50,0 (0,64)	1655	0,10	0,48	0,70
Acetylrhodalgin (II)	$C_{22}H_{20}O_{12}$	223–224	+69,2 (0,8)	1647, 1680	0,12	0,60	0,85
Diacetylrhodalgin (III)	$C_{24}H_{22}O_{13}$	208–209	– 5,0 (1,6)	1660, 1745	0,23	0,75	0,90
Triacetylrhodalgin (IV)	$C_{26}H_{24}O_{14}$	230–231	–20,1 (0,68)	1655, 1710, 1755	0,23	0,80	0,93
Alginin (V)	—	212–214	—	1650, 1730	0,12	0,43	0,18
Rhodalgidin (VI)	—	235–237	—	1650, 1750	0,27	0,52	0,0

*1) 15% AcOH; 2) 60% AcOH (FN-15 paper); 3) chloroform–methanol (3 : 1); Woelm silica gel.

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420 nm) shows 4'-substitution, which was also confirmed by the reaction with Mg +HCl with the subsequent addition of an excess of $NaHCO_3$ [1]. The behavior of the glycoside (VI) differed only with the addition of an excess of NaOAc (273 nm) which indicates 4',7-substitution.

The IR spectra of the glycosides differed considerably: in addition to the band of the carbonyl of a γ-pyrone in compounds (II-VI), bands appeared which were due to additional carbonyl groups (see Table 1).

According to the NMR spectra of the TMS ethers (in CCl_4), compounds (I-V) are monoglycosides, while (II) contains one acetoxy group (singlet at 2.05 ppm), (III) contains two (1.97 and 1.80 ppm) and (IV) contains three acetoxy groups (1.97, 1.92, and 1.84 ppm) bound to the carbohydrate moiety of the molecule. Compound (VI) is a diglycoside.

Thus, all the compounds isolated are new glycosides of herbacetin for which we propose the following names: herbacetin 4'-arabinoside (I) – rhodalgin; herbacetin 4'-monoacetylarabinoside (II) – acetylrhodalgin, herbacetin 4'-diacetylxyloside (III) – diacetylrhodalgin; herbacetin 4'-triacetylxyloside (IV) – triacetylrhodalgin; herbacetin 4'-glucuronide (V) – alginin; and the herbacetin 4',7-diglycoside (VI) – rhodalgidin.

The flavonoids are accompanied by substances of nonflavonoid nature; compound (VII) with the composition $C_{25}H_{50}O$, mp 66-68°C is, according to its spectrum, an alkanone or a mixture of alkanones mainly of linear structure, and (VIII) was identified as D-mannose.

LITERATURE CITED

1. L. Hörhammer and R. Hansel, Arch. Pharm., 287/59, No. 1, 36 (1954).