THE STRUCTURE OF THE FLAVONOIDS FROM Rhodiola algida. II

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We have previously reported the isolation from the roots of Rhodiola algida (Ledeb.) Risch. et May of six new flavonoid glycosides [1]. In the present paper we give information on the determination of the structures of four of them: rhodalgin (I), acetylrhodalgin (II), diacetylrhodalgin (III) and triacetylrhodalgin (IV). The acetylation of the glycosides (I) and (II) gave the same heptaacetate (V) with the composition $C_{34}H_{32}O_{18}$, mp 190-191°C; compounds (III) and (IV) also gave the same heptaacetate (VI) with the composition $C_{34}H_{32}O_{18}$, mp 114-115°C. This confirmed that the initial compounds (II), (III), and (IV) contained the acetyl groups the presence of which had been shown by IR and NMR spectroscopy [1] in the carbohydrate part of the molecule.

The aglycone in all the compounds is herbacetin (3,4',5,7,8-pentahydroxyflavone (VIII)). Acid hydrolysis of all the glycosides took place rapidly and without the migration of the 8-OH group into position 6 that is frequently observed for 5,7,8-trihydroxyflavonoids (for example, in the hydrolysis of 3',4',5,7,8-pentahydroxyflavone 7-glucoside [2]). The absence of migration was shown by the fact that in the NMR spectra of the trimethylsilyl ethers (TMS ethers) of the glycosides and of the aglycone the singlet of the C_6 proton has the same chemical shift (CS), δ 6.06 ppm. The acid hydrolysis of (I) and (II) liberated L-arabinose, and that of (III) and (IV) liberated D-xylose.

The NMR spectra of the glycosides taken in DMSO showed the signal of a free 5-OH group at 12.3 ppm. On irradiation with UV light, the substances possess a bright yellow fluorescence, which shows the presence of a free 3-OH group. The UV spectra (maxima at 377, 327, and 272 nm) are characteristic for flavonols. The presence of 4'- and 7-OH groups was shown by the bathochromic shift of the long wave (20nm) and short wave (8 nm) maxima in the presence of sodium acetate. The absence of a similar shift in the spectrum with boric acid (378 nm) shows the absence of an ortho-dihydroxy grouping. With $AlCl_3$, maxima appeared in the spectrum at 436, 358, 312 (shoulder), and 272 nm. The nature of the curves and the position of the maxima coincide with the characteristics given for the 8-methyl ether of herbacetin [3]. However, in view of the stability of substances (I-IV) on the addition of sodium methoxide (the maxima at 420, 325, and 282 nm remain unchanged for 5 min) we assumed that in our glycosides the carbohydrate moiety is attached to position 4' of the aglycone [1]. Results of further study did not confirm this hypothesis.

Methylation of the glycosides with diazomethane and subsequent acid hydrolysis led to the formation of 5,8-dihydroxy-3,4',7-trimethoxyflavone (IX). For comparison, 5-hydroxy-3,4',7,8-tetramethoxyflavone (VIII) was obtained by the methylation of (VII). The structures of (VIII) and (IX) were shown by NMR and mass spectroscopy. It is known that the resonance of methoxy groups depends strongly on the solvent [4, 5]. In the spectrum of compound (VIII), the replacement of $CDCl_3$ by C_6D_6 caused a shift in the signals, which were assigned in the following way on the basis of literature information: 3.71 ppm (3- and 8-OMe), 3.28 ppm (4'-OMe), and 3.21 ppm (7-OMe). For (IX) the following groups were found: 3-OMe (3.73 ppm), 4'-OMe (3.27 ppm), and 7-OMe (3.08 ppm).

It is also known from the literature that in the mass spectra of methoxy derivatives of highly hydroxylated flavonols strong peaks of $(M - R)^+$, corresponding to the loss of a substituent R from an oxygen atom at C_6 or C_8 are diagnostic; 3-OMe substituents are eliminated preferentially in the form of acetyl radicals [6, 7]. The mass spectra of compounds (VIII) and (IX) confirm the structures suggested for them: the $(M - CH_3)^+$ ion shows the presence of an 8-OMe group in (VIII) and the $(M - H)^+$ ion the presence of an 8-OH group in (IX).

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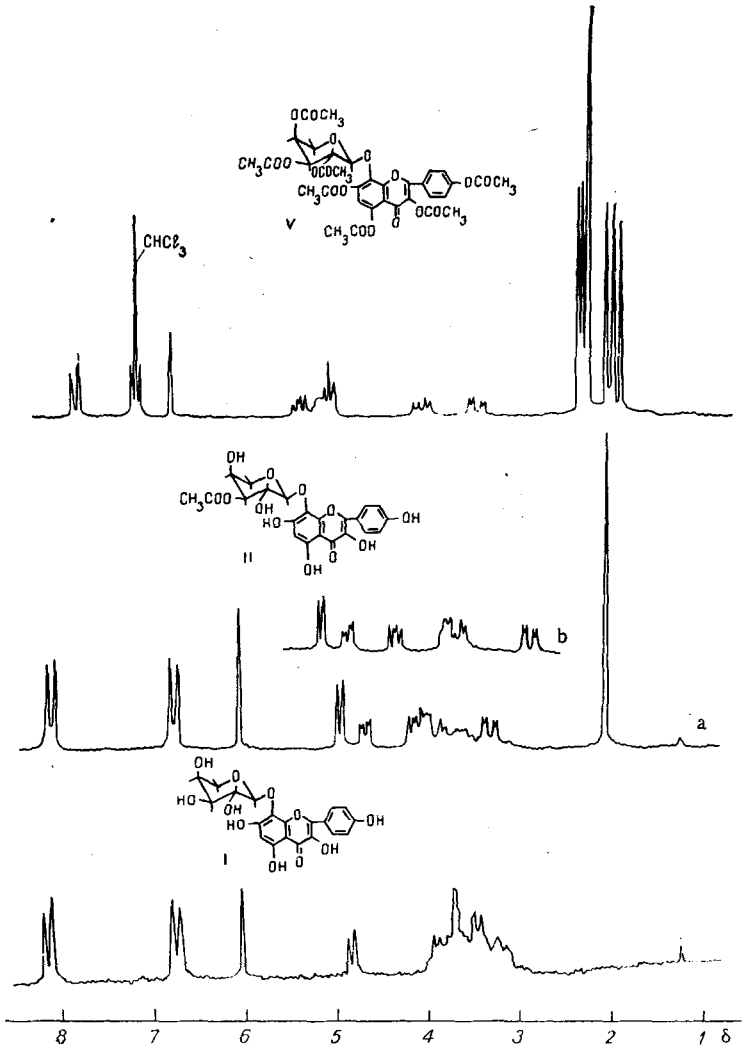


Fig. 1. NMR spectra of the TMS ether of rhodalgin (I) in CCl_4, of the TMS ether of acetylrhodalgin (II) in CCl_4 (a) and in C_6D_6 (b), and of the heptaacetate (V) in $CDCl_3$.

Important information on ring B is given by the fragment of the phenyl side chain (m/e 135), confirming the presence of a 4'-OMe group in (VIII) and (IX) and therefore of a free 4'-OH group in the glycosides. The results obtained show that in the glycosides the sugars are attached in position 8 of herbacetin, which is also confirmed by a gossypetone test for a p-dihydroxy grouping that is negative for the glycosides and positive for the aglycone and the trimethyl ether (IX).

In the mass spectra of all the glycosides, the strongest peaks are those of the aglycone (M^+ 302) and of its fragments – m/e 273, 121, etc. However, for (II), (III), and (IV) molecular ions of low intensity with m/e 476, 518, and 560, respectively, were obtained. Their spectra lack the ions characteristic for the decomposition of furanosides for which the most characteristic feature is the cleavage of the C_4-C_5 bond, producing strong ions without side chains [8, 9]. In our case, the side chain may be either $-CH_2OH$ or $-CH_2OCOCH_3$. Nevertheless, the ions $(M-31)^+$ are absent from the spectra of compounds (II), (III), and (IV). We must mention the ion with m/e 344 present is the spectrum, which can probably be formed in the case of pyranosides by cleavage of the C_1-C_2 and C_4-C_5 bonds. The pyranose form of the sugars is shown by the multiplicity of the signals of the methylene protons in the NMR spectra and by the large distance between the H-5a and H-5b signals (Table 1 and Figs. 1 and 2). The values of the coupling constants of the protons of the sugars in (I-VI) and the values of Δ_{H_5a,H_5e} coincide with those given in the literature for arabinopyranosides and xylopyranosides [10, 11], while in the furanosides the CSs of the protons at C_5 are approximately the same and they form a multiplet [12-14]. Thus, in the glycosides (I-IV) and their acetates (V and VI), the sugar is present in the pyranose form.

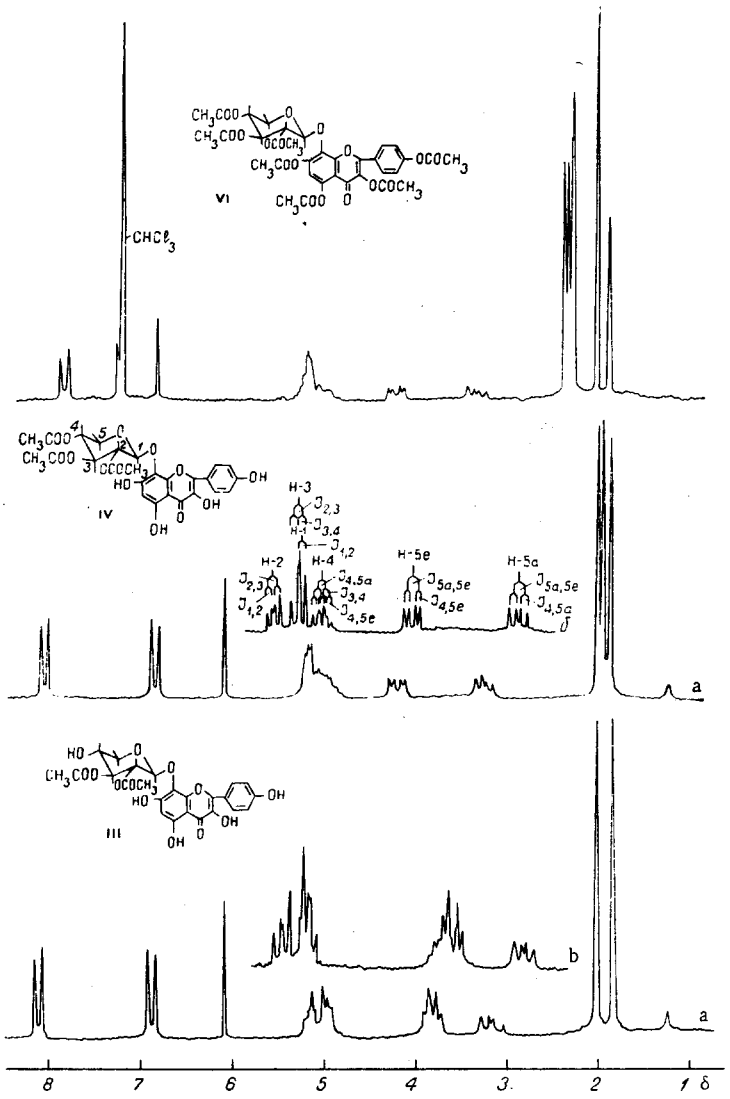
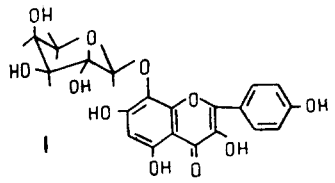


Fig. 2. NMR spectra of the TMS ethers of diacetylrhodalgin (III) and of triacetylrhodalgin (IV) in CCl_4 (a) and C_6D_6 (b), and of the heptaacetate (VI) in $CDCl_3$.

In the NMR spectrum of the TMS ether of rhodalgin in CCl_4 (Fig. 1, I), in addition to the signals of the aromatic protons, which are the same for all the glycosides (8.1 ppm, H-2',6'; 6.8 ppm, H-3',5'; 6.06 ppm, H-6), there is a multiplet of 5 carbohydrate protons and a doublet of the anomeric proton at δ 4.84 ppm. For the L-arabinopyranose in (I) and (II) the axial–axial spin–spin coupling constant (J = 6 Hz) of the anomeric proton can be realized only in the case of the α anomer in the C1 conformation. Consequently, rhodalgin has the structure I.

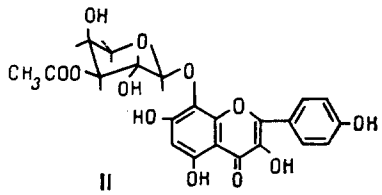


The spectrum of the TMS ether of acetylrhodalgin in CCl_4 (see Fig. 1, IIa) differs from (I) by the singlet of an acetoxy group (2.05 ppm) and the quartet of the hemiacyl proton (4.7 ppm). In C_6D_6 solution, the signals of H-2 and of H-5a can also be seen (see Fig. 1, II, and Table 1). The splitting constants of the hemiacyl proton (8 and 3 Hz) show that it is axial and interacts with the neighboring axial and equatorial protons. This is possible only if the acetyl group is attached to position 3 of the arabinose. Thus, acetylrhodalgin has structure II.

TABLE 1. Chemical Shifts and Coupling Constants of the Carbohydrate Protons

Compound	Solvent	H-1	H-2	H-3	H-4	H-5e	H-5a	
I	CCl_4	d 4,84 $J_{1,2}=6$	Multiplet 3,1 –4,0 (5H)					—
II	CCl_4	d 5,00 $J_{1,2}=6$	dd 4,14 $J_{1,2}=6$ $J_{2,3}=8$	dd 4,7 $J_{3,4}=3$ $J_{2,3}=8$	Multiplet 3,2–4,1 (3H)			2,05 (3H)
	C_6D_6	d 5,20 $J_{1,2}=6$	dd 4,38 $J_{1,2}=6$ $J_{2,3}=8$	dd 4,9 $J_{3,4}=3$ $J_{2,3}=8$	Multiplet 3,6–3,9 (2H)		dd 2,9 $J_{5a,5e}=12$ $J_{4,5a}=2$	1,80 (3H)
III	CCl_4	Multiplet 4,8–5,2 (3H)			Multiplet 3,7–3,9 (2H)		dd 3,15 $J_{5a,5e}=13$ $J_{4,5a}=8$	1,97 (3H) 1,80 (3H)
	C_6D_6	d 5,17 $J_{1,2}=7$	dd 5,43 $J_{1,2}=7$ $J_{2,3}=9$	t 5,15 $J_{2,3}=J_{3,4}=9$	Multiplet 3,45–3,8 (2H)		dd 2,80 $J_{5a,5e}=13$ $J_{4,5a}=8$	1,71 (3H) 1,68 (3H)
IV	CCl_4	Multiplet 4,8–5,2 (4H)				dd 4,17 $J_{5a,5e}=13$ $J_{4,5e}=5$	dd 3,22 $J_{5a,5e}=13$ $J_{4,5a}=7$	1,97 (3H) 1,92 (3H) 1,84 (3H)
	C_6D_6	d 5,22 $J_{1,2}=7$	dd 5,54 $J_{1,2}=7$ $J_{2,3}=9$	t 5,27 $J_{1,3}=J_{3,4}=9$	o 5,0 $J_{4,5e}=5$ $J_{3,4}=9$ $J_{4,5a}=8$	dd 4,02 $J_{5a,5e}=13$ $J_{4,5e}=5$	dd 2,85 $J_{5a,5e}=13$ $J_{4,5a}=8$	1,80 (6H) 1,42 (3H)
V	$CDCl_3$		dd 5,42 $J_{1,2}=6$ $J_{2,3}=8$	H-1, H-3, H-4- Multiplet 5,0–5,3 (3H)		dd 4,06 $J_{5a,5e}=13$ $J_{4,5e}=5$	dd 3,46 $J_{5a,5e}=13$ $J_{4,5a}=3$	3,05 (3H) 1,98 (3H) 1,90 (3H)
VI	$CDCl_3$	Multiplet 4,8–5,3 (4H)				dd 4,18 $J_{5a,5e}=13$ $J_{4,5e}=5$	dd 3,30 $J_{5a,5e}=13$ $J_{4,5a}=7$	1,99 (6H) 1,86 (3H)

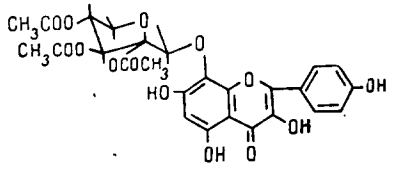
*The chemical shifts are given in ppm on the δ scale (internal standard HMDS) and the coupling constants in Hz; d) doublet; dd) quartet; t) triplet; c) octet.



II

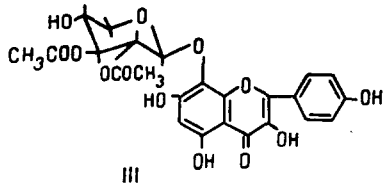
In the NMR spectrum of the TMS ether of triacetylrhodalgin in CCl_4 (Fig. 2, IVa), there are the signals of three acetoxy groups (1.97, 1.92, and 1.84 ppm), and the signals of H-5a and H-5e can be seen, the others carbohydrate protons forming a multiplet. In deuterobenzene (see Fig. 2, IVb) it is easy to assign the signals of all the xylose protons, the nature of the splitting of which greatly resembles the multiplicity of the analogous protons in 1,2,3,4-tetra-O-acetyl-N-benzyloxycarbonyl-α-D-xylopyperidinose [11] and in the tetraacetate of 1-thio-β-D-xylanopyranose [10]. For the D-xylopyranose in (III) and (IV) (see Fig. 2), a doublet of the anomeric proton with $J_{1,2}$ = 7 Hz is possible only for the β anomer in the C1 conformation. Consequently, the structure of triacetylrhodalgin corresponds to structure (IV).

Diacetylrhodalgin contains two acetoxy groups (see Fig. 2, IIIa – singlets at 1.97 and 1.80 ppm). In CCl_4, the signals of the anomeric and hemiacyl protons form a multiplet in the 4.8-5.2 ppm region.



IV

In a comparison of the NMR spectra of the TMS ethers of diacetylrhodalgin and triacetylrhodalgin taken in deuterobenzene (see Fig., IIIb and IVb), it can be seen that in the weak-field region there is no H-4 multiplet for diacetylrhodalgin. This shows that the 4-OH group of the xylose is free in diacetylrhodalgin, and it has the structure III.



III

EXPERIMENTAL

The IR spectra were taken on UR-10 and UR-20 spectrometers in paraffin oil, the UV spectra on a Hitachi EPS-3T instrument in methanol with the addition of diagnostic reagents, the NMR spectra on a Varian HA-100D spectrometer at 100 MHz (internal standard HMDS), and the mass spectra on a Varian CH-8 instrument with the direct introduction of the sample at 75 eV and a recording temperature for the glycosides of 200-218°C and for the aglycones of 100-170°C. The melting points were determined on a Kofler block, and the $[\alpha]_D$ values on a A1-EPL polarimeter. The purity of the substances was checked by TLC on Woelm silica gel in the chloroform–methanol (3 : 1 and 6 : 1) and benzene–ethyl acetate (3 : 1) systems and by PC on FN-15 paper in 15% and 60% AcOH.

The elementary analyses corresponded to the calculated figures.

Isolation of the Glycosides. The comminuted roots of Rhodiola algida were extracted with methanol, the aqueous solution after the ethanol had been distilled off was extracted with other, and the residue from the evaporation was deposited on polyamide and was chromatographed in a chloroform–methanol gradient system. Chloroform eluted compound (IV), chloroform containing 2% of methanol eluted a mixture of (III) and (IV), chloroform with 5% ethanol eluted a mixture of (II) and (III), and chloroform with 7% methanol eluted (I). On rechromatography under the same conditions and repeated recrystallization from ethanol and methanol, the bright yellow pure substances were obtained.

Rhodalgin (I), $C_{20}H_{18}O_{11}$, mp 239-240°C, $[\alpha]_D^{20}$ + 50.0° (c 0.64; MeOH), ν_{CO} 1655 cm^{-1}; λ_{max} 272, 327, 376 nm. The NMR spectrum is given in Fig. 1.

Acetylrhodalgin (II), $C_{22}H_{20}O_{12}$, mp 223-224°C, $[\alpha]_D^{20}$ 69.2° (c 0.8; MeOH), ν_{CO} 1647, 1680 cm^{-1}; λ_{max} 272, 327, 377 nm. The NMR spectrum is given in Fig. 1. Mass spectrum: m/e (int., %) M^+ 476 (04), 344 (2), 302 (100), 273 (7), 121 (22).

Diacetylrhodalgin (III), $C_{24}H_{22}O_{13}$, mp 208-209°C, $[\alpha]_D^{20}$ – 5.0° (c 1.6; MeOH), ν_{CO} 1660, 1745 cm^{-1}; λ_{max} 272, 327, 274 nm. The NMR spectrum is given in Fig. 2. Mass spectrum: M^+ 518 (0.4) 344 (5), 302 (100), 273 (12), 121 (30).

Triacetylrhodalgin (IV), $C_{26}H_{24}O_{14}$, mp 230-231°C, $[\alpha]_D^{20}$ – 20.1° (c 0.68; MeOH), ν_{CO} 1655, 1710, 1755 cm^{-1}; λ_{max} 272, 327, 375 nm. The NMR spectrum is given in Fig. 2. Mass spectrum: M^+ 560 (0.5), 344 (6) 302 (100), 273 (8), 121 (32).

Preparation of the Trimethylsilyl Ethers. A solution of 30 mg of one of the glycosides in 0.5 ml of pyridine (anhydrous) was treated with 0.3 ml of chlorotrimethylsilane and 0.3 ml of hexamethyldisilazane. The mixture was left in a closed flask at 20°C for 20-30 min, and then the excess of the reagents was distilled off, CCl_4 was added, the precipitate was separated off and the filtrate was evaporated in vacuum until the residue no longer smelt of pyridine. The TMS ethers of the glycosides (I-IV) and of the aglycone were obtained in this way for recording the NMR spectra in CCl_4 and C_6D_6.

Acetylation of the Glycoside. A mixture of 20 mg of (I) (or (II)) 0.3 ml of pyridine, and 0.7 ml of acetic anhydride was kept at 20°C for 24 h. This was poured into ice water, and the precipitate that deposited was separated off, washed with water, and recrystallized several times from ethanol. This gave the heptaacetate (V) with the composition $C_{34}H_{32}O_{18}$, mp 190-191°C, ν_{CO} 1662, 1745, 1780, 1790 cm^{-1}. Its NMR spectrum is given in Fig. 1.

In a similar manner, (III) and (IV) gave the octaacetate (VI) with the composition $C_{34}H_{32}O_{18}$, mp 114-115°C, ν_{CO} 1660, 1770, 1790 cm^{-1}. The NMR spectrum is given in Fig. 2.

Acid Hydrolysis. A mixture of 10-20 mg of a glycoside (I, II, III, or IV) and 2-3 ml of 2% HCl was heated at 90°C for 5-15 min. The precipitate that deposited was filtered off and recrystallized from ethanol. The aglycone herbacetin (VII), $C_{15}H_{10}O_7$, was obtained with mp 278-280°C, λ_{max} 226, 278, 330, 385 nm. NMR spectrum of the TMS ether in CCl_4: 8.0 ppm (H-2',6'), 6.76 ppm (H-3',5'), 6.07 ppm (H-6). Mass spectrum:

m/e (int., %), M^+ 302 (100), $(M-CO)^+$ 273 (12), 168 (12), 121 (27). Pentaacetate of herbacetin, $C_{25}H_{20}O_{12}$, mp 185-186°C. NMR spectrum in $CDCl_3$: 7.70 ppm (H-2',6'), 7.18 ppm (H-3',5'), 6.9 ppm (H-6), 2.28-2.40 ppm (5 CH_3CO).

The filtrate after the separation of the aglycone was neutralized on Dowex-2 ion-exchange resin (HCO_3^- form), concentrated, and chromatographed with markers in several solvent systems on paper and silica gel, the spots being revealed with a solution of $AgNO_3$ + NH_4OH. Arabinose was found in the hydrolyzates of compounds (I) and (II) and xylose in those of (III) and (IV).

Methylation. A. Preparation of 5-Hydroxy-3,4',7,8-tetramethoxyflavone (VIII). A solution of 50 mg of herbacetin (VII) in 5 ml of absolute methanol was mixed with an excess of an ethereal solution of diazomethane and the mixture was left overnight. Then the solvents were distilled off, the residue was dissolved in acetone, and the solution was filtered through a column of Al_2O_3 (1 g). After evaporation of the acetone, the residue was recrystallized from ethanol. This gave yellow crystals of substance (VIII) $C_{19}H_{18}O_7$, mp 167-168°C. NMR spectrum in $CDCl_3$: singlets of four OCH_3 groups (3.94, 3.90, 3.88, 3.96 ppm), singlet of H-6 located at δ = 6.4 ppm; in C_6D_6: 3.71 ppm (6H), 3.28 ppm (3H), 3.21 ppm (3H). Mass spectrum: m/e (int., %) M^+ 358 (70), $(M-CH_3)^+$, 343 (100), 329 (5), 315 (4), 135 (13).

Monoacetate $C_{21}H_{20}O_8$, mp 169-170°C. NMR spectrum in $CDCl_3$: 5-OAc, singlet at 2.5 ppm; H-6, singlet at 6.67 ppm. Mass spectrum: M^+ 400 (12), 358 (100), 343 (100), 329 (5), 315 (4), 135 (13).

B. Preparation of 5,8-Dihydroxy-3,4',7-trimethoxyflavone (IX). A solution of 50 mg of (I) (or II, III, or IV) in methanol was treated with an excess of diazomethane in ether and the mixture was left overnight. After elimination of the solvents, the residue was heated with 2 ml of 2% HCl for 30 min. The precipitate that deposited was separated off and dissolved in acetone, and the solution was filtered through 1 g of Al_2O_3. Then, substance (IX), $C_{18}H_{16}O_7$, mp 202-204°C was obtained as in the preparation of (VII). NMR spectrum in $CDCl_3$: singlets of three OMe groups (3.9, 3.82, 3.8 ppm), singlet of H-6 (6.35 ppm); in CD_6: 3.73 ppm (3H), 3.27 ppm (3H), 3.08 ppm (3H). Mass spectrum: M^+ 344 (100), $(M-H)^+$ 343 (50), $(M-CH_3CO)^+$ 301 (55), 135 (15).

The diacetate, $C_{22}H_{20}O_9$, mp 232-234°C. NMR spectrum in $CDCl_3$: 5-OAc singlet at 2.5 ppm; 8-OAc, singlet at 2.45 ppm; H-6, singlet at 6.65 ppm. Mass spectrum: M^+ 428 (20), 385 (16), 343 (100), 300 (17), 135 (15).

SUMMARY

New flavonoid glycosides have been obtained from the roots of Rhodiola algida: rhodalgin (I), composition $C_{20}H_{18}O_{11}$, mp 239-240°C; acetylrhodalgin (II) $C_{22}H_{20}O_{12}$, mp 223-224°C; diacetylrhodalgin (III), $C_{24}H_{22}O_{13}$, mp 208-209°C; and triacetylrhodalgin (IV), $C_{26}H_{24}O_{14}$, mp 230-231°C.

It has been established that they have the following structures: (I), 3,4',5,7,8-pentahydroxyflavone 8-O-α-L-arabinopyranoside; (II), 3,4',5,7,8-pentahydroxyflavone 8-O-(3"-O-acetyl-α-L-arabinopyranoside; (III), 3,4',5,7,8-pentahydroxyflavone 8-O-(2",3"-di-O-acetyl)-β-D-xylopyranoside; and (IV), 3,4',5,7,8-pentahydroxyflavone 8-O-(2",3"4"-tri-O-acetyl)-β-D-xylopyranoside. The α-L-arabinopyranose and β-D-xylopyranose are present in these compounds in the C1 conformations.

In the performance of this investigation, the authors consulted O. S. Chizhov, and M. B. Zoltarev (N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR) and V. I. Sheichenko (All-Union Institute of Medicinal plants).

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GALLOMYRICITRIN – A NEW ACYLATED FLAVONOID FROM *Sedum selskianum*

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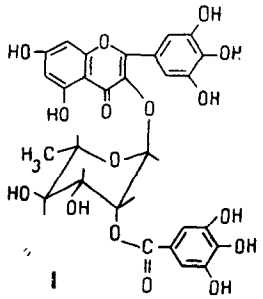
We have previously reported the isolation from the epigeal part of Sedum selskianum Rgl. et Mask. of the flavonoids myricitrin [1] and brassidin, and a new compound, which we called gallomyricitrin [2].

Gallomyricitrin (I) has the composition $C_{28}H_{24}O_{16} \cdot 2H_2O$, mp 214-216°C, $[\alpha]_D^{20} -40°$ (c 0.6; methanol). The acid hydrolysis of (I) gave the aglycone myricetin, L-rhamnose, and gallic acid. UV spectroscopy showed that the myricetin has one substituent in position 3. The acetylation of (I) gave a decaacetate (II) with the composition $C_{48}H_{44}O_{26}$, mp 136-138°C.

The NMR spectrum of (II) (Fig. 1) showed the signals of H-2',6' of myricetin and of H-2''',6''' of gallic acid (two-proton singlets at 7.78 and 7.68 ppm), and two doublets with J = 2.5 Hz of H-6 (6.8 ppm) and H-8 (7.3 ppm) of myricetin. In the 0.95-ppm region there is a doublet (J = 6 Hz) of the CH_3 group of rhamnose; the other protons of rhamnose resonate in the 3.3-5.9 ppm region: H-1'' and H-2'' as a multiplet with its center at 5.92 ppm, H-3'' as a quartet at 5.26 ppm ($J_{2,3}$ = 3 Hz, $J_{3,4}$ = 10 Hz), H-4'' as a triplet at 4.92 ppm ($J_{3,4} = J_{4,5}$ = 10 Hz), and H-5'' as a quartet at 3.32 ppm ($J_{5,6}$ = 6 Hz, $J_{4,5}$ = 10 Hz). Among the signals of the ten acetoxy groups two signals stand out at δ 1.95 and 1.98 ppm which are due to the carbohydrate part of the molecule and a singlet of the 5-OAc flavonoid part of the molecule (2.4 ppm); the other seven, aromatic, acetyl groups resonate in the 2.26-2.32 ppm region.

The results of a comparison of the chemical shifts and of the coupling constants of the carbohydrate protons of the TMS other (I) and the acetate (II) (see Fig. 1) with the values obtained for the acetates and TMS ethers of the 3-O-α-L-rhamnopyranosides of myricetin and quercetin permit the conclusion that in compounds (I) the L-rhamnose has a pyranose ring and the 1C conformation. A small coupling constant of the anomeric proton is possible for both the α and the β anomers; however, the magnitude and sign of the angle of optical rotation excludes the β form. The presence of only two singlets of aliphatic AcO groups in the spectrum of (II) and also of the signal of the hemiacyl proton (triplet at 5.6 ppm) in the TMS ether of (I) show that the gallic acid is attached to the rhamnose, and the spin–spin coupling constant in the triplet ($J_{1,2}$ = 2 Hz, $J_{2,3}$ = 2.5 Hz) enables it to be assigned to H-2'' of rhamnose. Thus, the gallic acid acylates the hydroxyl in position 2 of the rhamnose. On the basis of the facts presented, the following structure can be proposed for gallomyricitrin:



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