The acetylation of (I) with acetic anhydride in pyridine yielded a monoacetate $C_{26}H_{36}O_7$ (III) with mp 162-163°C, in the PMR spectrum (in $CDCl_3$) of which there was a shift on the signal from C_6'—H. The dehydration of foliferin in 10% ethanolic sulfuric acid led to an anhydro derivative $C_{24}H_{30}O_4$ (IV) with mp 154-155°C, $[\alpha]_D^{21}$ +217° (c 1.84; chloroform), which was an epimer of feropolidin [4].

On the basis of the facts presented, structure (I) is suggested for foliferin.

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STRUCTURES OF FLAVONOIDS FROM *Rhodiola algida*. III

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UDC 547.972

We have previously reported the isolation from *Rhodiola algida* Ledeb. (Fisch. et May.) of a number of flavonoid glycosides [1] and the determination of the structure of four of them [2]. In the present paper we give information for establishing the structure of the alginin (I) isolated previously and of two new compounds now isolated which have been called rhodalin (II) and acetylrhodalin (III).

The acid hydrolysis of all three compounds (I-III) gave the same aglycone herbacetin (3,4',5,7,8-pentahydroxyflavone), which was identified by its PMR, UV, and mass spectra and direct comparison with an authentic sample. The carbohydrate moiety in compound (I) consisted of glucuronic acid (obtained on cleavage with β-glucuronidase), and in compounds (II) and (III) the herbacetin was glycosidated with xylose. The UV spectra of compounds (I-III) in methanol with diagnostic reagents were practically identical and did not differ from the spectra of the herbacetin 8-glycosides described previously [2].

In the PMR spectrum of the TMS ether of alginin (I) there were the signals of a 4'-substituted ring B (two doublets with J = 9 Hz at 8.14 and 6.82 ppm) and a H-singlet at 6.08 ppm. The anomeric proton gave a signal in the form of a doublet with J = 6.5 Hz at 5.0 ppm, and the other protons of the glucuronic acid formed a group of overlapping signals in the 3.9-3.3-ppm region. The IR spectrum of compound (I) had a broad band with its maximum at 1730 cm^{-1}, the appearance of which was due to the carbonyl group of the glucuronic acid. The facts given permitted the structure of 3,4',5,7,8-pentahydroxyflavone 8-O-β-D-glucopyranoside to be suggested for alginin (I).

Compounds (II), mp 270-274°C, and (III), mp 276-279°C, were obtained from the mother liquors and certain fractions after the isolation of rhodalgin and acetylrhodalgin [1]. They were separated by fractional recrystallization from methanol, their purity being checked from the results of acid hydrolysis (absence of arabinose), since the pairs of glucosides rhodalgin—rhodalin and their corresponding monoacetyl derivatives are difficult to separate on chromatograms.

The PMR spectrum of rhodalgin (II) in deuteropyridine includes the signals of five protons of herbacetin: 9.0 ppm (d, 9 Hz, H-2',6'), 7.3 ppm (d, 9 Hz, H-3',5'), and 6.7 ppm (s, H-6). In the stronger field there is a doublet with J = 7 Hz at 5.3 ppm, which is characteristic for the anomeric proton of β-D-xylose, the remaining protons of which form a group of

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Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 519-520, July-August, 1978. Original article submitted February 28, 1978.

0009-3130/78/1404-0443$07.50

signals in the 4.6-3.6-ppm region. The acetylation of compounds (II) and (III) gave the same product, identical with herbacetin 8-O-β-D-xylopyranoside heptaacetate [2] in its melting point, PMR spectrum, and chromatographic mobility. On the basis of the facts presented, the structure of 3,4',5,7,8-pentahydroxyflavone 8-O-β-D-xylopyranoside is proposed for rhodalin (II).

The IR spectrum of compound (II) showed, in addition to the stretching vibrations of the CO group of herbacetin (1658 cm^{-1}) the band of an ester group at 1707 cm^{-1}. The PMR spectrum of (III) in deuteropyridine differed from that of (II) by the presence of a three-proton singlet (1.90 ppm) of a CH_3COO group attached to the carbohydrate part of the molecule and by the appearance in the weak field of the signal of a hemiacyl proton (triplet at 5.64 ppm).

The spin–spin coupling constants of the anomeric proton (7 Hz) and of the hemiacyl protons ($J = J_1 = 9$ Hz) permit the following conclusion: the acetic acid residue acylates the 3"-OH group in the β-D-xylopyranose residue, since if the 2"-OH group were acylated the signal of the hemiacyl proton should have a single constant $J_{1,2} = 7$ Hz, and if the 4"-OH group were isolated this signal would appear in the form of a multiplet through interaction with H-3" and 2H-5" [2]. Consequently, acetylrhodalin (III) has the structure of 3,4',5,7,8-pentahydroxyflavone 8-O-(3"-O-acetyl-β-D-xylopyranoside).

The specificity of the enzyme system of *Rhodiola algida* must be mentioned: the seven flavonoid compounds of which the structure has been established are 8-glycosides of herbaceti and their diversity is due to the different carbohydrate residues, four of the glycosides containing acetylated arabinose and xylose.

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FLAVONOIDS OF *Hypericum hirsutum*

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UDC 547.972

We have investigated the herb *Hypericum hirsutum* L., family Gulliferae, collected in the flowering period in the environs of the town of Kursk.

The dried comminuted herb was exhaustively extracted with 96% ethanol. The extract was evaporated in vacuum to a syrupy consistency and was treated with hot water. The resinous substances were separated by filtration in vacuum. Ballast substances were eliminated with ether. The resulting extract was deposited on a column filled with polyamide sorbent. The column was washed with water and then with aqueous ethanol of increasing concentration. The eluates were analyzed with the aid of color reactions and paper chromatography. The fraction were dried in vacuum. This gave substances (I), (II), and (III) in the individual state.

The substances obtained were identified on the basis of the physicochemical properties of the initial compounds and also the products of their transformation, IR and UV spectra, and the results of a comparison with authentic samples [1, 2].

Substance (I) formed a yellow crystalline powder with mp 310-312°C; $C_{15}H_{10}O_7$. In the products of alkaline cleavage were found protocatechuic acid and phloroglucinol. It was established that substance (I) is 3,3',4',5,7-pentahydroxyflavone, or quercetin.

Substance (II) formed pale yellow acicular crystals with mp 190-191°C, $C_{27}H_{30}O_{16}$ $[\alpha]_D^{18}$ −38.6° (c 0.3; methanol). Substance (II) had a positive cyanidin reaction and a negative Bryant reaction [3]. On acid hydrolysis quercetin, L-rhamnose, and D-glucose were detected. Substance (II) was identified as quercetin 3-(6-α-L-rhamnopyranosyl-β-D-glucopyranoside), or rutin.

Kursk State Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 520, July-August, 1978. Original article submitted March 7, 1978.

 0009-3130/78/1404-0444$07.50