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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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.

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Substance (III) formed yellow acicular crystals with mp 237-238°C, $C_{21}H_{20}O_{12}$, the acid hydrolysis of which formed quercetin and D-galactose. It gave a positive cyanidin reaction but a negative Bryant reaction. Substance (III) was characterized as quercetin 3-O-β-D-galactoside, or hyperoside.

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FLAVONOIDS OF *Stachys inflata*

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The isolation from the epigeal part of *Stachys inflata* Benth. of stachyflaside has been reported previously [1].

In continuing investigations of the flavonoids of this plant we have isolated the total substances, which could not be separated by chromatography on paper in various systems. To establish the nature of the aglycones we hydrolyzed the combined glycosides with 5% sulfuric acid. The aglycones that deposited were separated on a column of polyamide sorbent (ratio of sorbent and mixture being separated 10:1) using as eluents chloroform–ethanol (98:2 and 80:2 by volume).

As a result, we obtained three aglycones: isoscutellarein ($C_{15}H_{10}O_6$, mp 252-256°C; for PMR spectrum, see below), scutellarein ($C_{15}H_{10}O_6$, mp 340-343°C), which was identified by comparison with that isolated previously [2] and 4'-O-methylisoscutellarein ($C_{16}H_{12}O_6$, mp 275-278°C) the structure of which was shown by comparison of the PMR spectra of the complete and 5-OH trimethylsilyl ethers [3], and also by the demethylation of the initial substance to isoscutellarein.

The spectrum of the TMS ether of 4'-O-methylisoscutellarein has the following signals: 7.80 ppm (H-2', H-6'), J = 8.5 Hz, 6.89 ppm (H-3', H-5'), J = 8.5 Hz, 6.39 ppm (H-3), 6.12 ppm (H-6), and 3.83 ppm (OCH_3-4'). The position of attachment of the methoxy group was shown by the production of 4-methoxybenzoic acid after alkaline degradation of the initial genin.

In the separation of the combined flavonoid glycosides under the same conditions as in the case of the aglycones, in addition to stachyflaside we isolated a substance with the composition $C_{27}H_{30}O_{16}$, mp 158-163°C; $[\alpha]_D^{20}$ −62° (c 0.1; ethanol), which we have called isostachyflaside. Like stachyflaside it is stable to enzymatic and alkaline hydrolysis [4, 5]. It was cleaved by 5% sulfuric acid into D-glucose, D-mannose, and an aglycone which on paper chromatography showed up in UV light before treatment with alkalis in the form of a dark spot. This shows the absence of a free OH group at C_3 of the flavonoid nucleus.

After treatment of the chromatogram with alkalis for 2-3 min, the spot of the aglycone began to fluoresce blue. In absolute ethanol with the addition of sodium ethanolate, both the glycoside and its genin formed no green coloration, and therefore it may be assumed that ring A does not have three free vicinal hydroxy groups.

As the PMR spectra showed, the genin forms a tetraacetyl derivative — signals with chemical shifts of 2.42 ppm (AcO at C_5) and 2.33 ppm (AcO — $C_{4',7,8}$), and signals of the chemical shifts of aromatic protons at 7.74 ppm (H-2', H-6'), J = 8.5 Hz, 7.26 ppm (H-3', H-5'), J = 8.5 Hz, 6.59 ppm (H-3), and 6.97 ppm (H-6), which shows the 4',5,7,8- type of substitution

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