THE STRUCTURE OF FOLIFERIN

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Continuing a study of the coumarins of the roots of *Ferula foliosa* Lipsky by column chromatography on KSK silica gel we have isolated a coumarin derivative with the composition $C_{24}H_{34}O_6$ (mol. wt. 418) with mp 240-241°C, $[\alpha]_D^{21}$ +128° (c 0.39; pyridine) which has been called foliferin [1]. The IR spectrum of the substance has maxima at 220, 244, 255, 290, and 328 nm (log ε 4.12, 3.46, 3.26, 3.85, 4.18), which are characteristic for 7-hydroxy-substituted coumarin derivatives, and the IR spectrum has absorption bands at 3510-3610 cm^{-1} (—OH), 1725 cm^{-1} (C=O of an α-pyrone), and 1620, 1560, 1515 cm^{-1} (aromatic nucleus).

The mass spectrum of (I) contains the peaks of ions with m/e 400 $(M - H_2O)^+$, 383 $(M - H_2O - 17)^+$, 238 $(M - ArOH - H_2O)^+$, 221 $(M - ArOH - H_2O - 17)^+$, 203 $(M - ArOH - 2H_2O - 17)^+$ and 162 $(ArOH)^+$, which are characteristic for terpenoid coumarins [2, 3]. The peaks of ions with m/e 238 and 162 show that the terpenoid part of foliferin has the composition $C_{15}H_{29}O_3$.

The absence from the IR spectrum of (I) of the absorption bands of an additional carbony group and a double bond and also from the PMR spectrum (Fig. 1) of signals from olefinic and epoxide protons and of a methyl group on a double bond shows that the terpenoid part of folif erin has a monocyclic structure, and the three oxygen atoms are present in hydroxy groups.

A substance with such a structure — feropolol — has been isolated previously from *F. polyantha* (*Peucedanum polyanthum* Eug. Kor.).

A comparison of the PMR spectra taken in deuteropyridine showed that they differed only in the values of the CSs and half-widths of the signals of the protons at C_6' and C'_1-CH_2OAr.

The difference in the multiplicities and CSs of the signal of the C_6' proton of foliferi and feropolol show that they are epimeric at C_6' and in (I) the hydroxy group has the equatorial orientation. This was confirmed by the preparation of a monoketone of foliferin with the composition $C_{24}H_{32}O_6$ (II), mp 225-226°C, which was identified spectrally and by a mixed-melting point as feropolone [4].

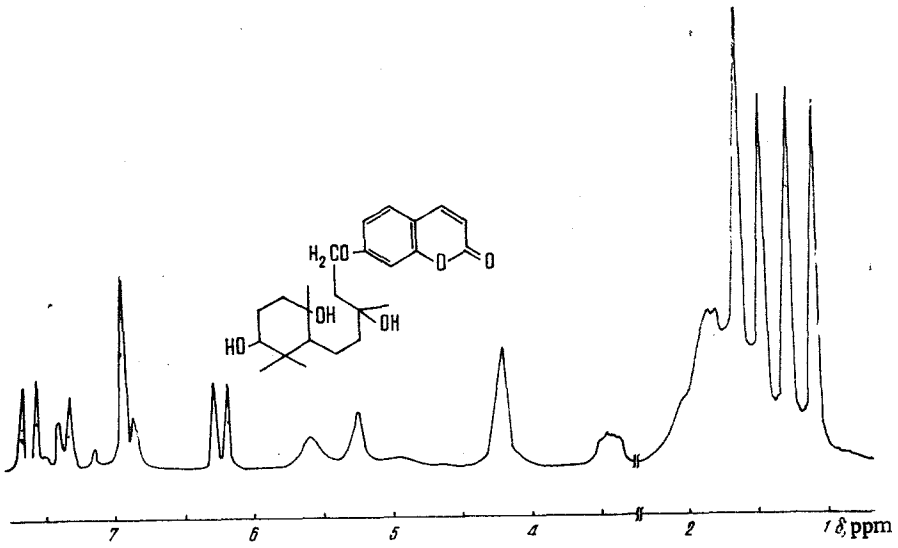

Fig. 1. NMR spectrum of foliferin (C_5D_5N).

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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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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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