STUDY OF THE STRUCTURE AND STEREOCHEMISTRY OF FLAVONOID O-ARABINOSIDES AND XYLOSIDES WITH THE AID OF PMR SPECTROSCOPY

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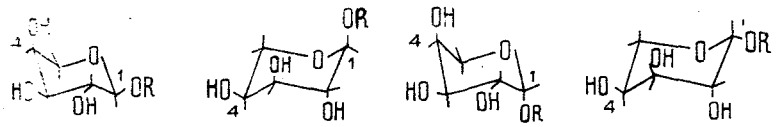
The considerable advances of the last few years in the structural analysis of flavonoid compounds is largely due to the use of modern physicochemical methods, especially proton magnetic resonance [1]. However, some questions of the structure of flavonoid glycosides, especially arabinosides and xylosides, have been studied inadequately. This circumstance has induced us to subject these substances to a more detailed investigation with the aim of elucidating correlations between the parameters of the PMR spectra and questions of structure and stereochemistry. Here one of the main tasks was to search for a method permitting a choice to be made between the pyranose and furanose forms of the pentoses.

We have obtained the PMR spectra of a number of natural flavonoid O-arabinosides and O-xylosides, and also their full acetates and trimethylsilyl ethers (TMS ethers). We have studied two herbacetin 8-glycosides [2]: rhodalgin (I) (α-L-arabinopyranoside) and acetylrhodalgin II) (the 3"-O-acetyl-α-L-arabinopyranoside); three isomeric quercetin 3-glycosides [3]: guaiaverin (III) (the α-L-arabinopyranoside), polystachoside (IV) [the β-L-arabinopyranoside (some authors consider it to be the β-L-arabinofuranoside [4]), and avicularin (V) (the α-L-arabinofuranoside); and two kaempferol 3-glycosides [5]: juglanin (VI) (the α-L-arabinofuranoside) and coumaroyljuglanin (VII) (the 2"-O-p-coumaroyl-α-L-arabinofuranoside).

Among the xylosides studied there were four herbacetin 8-glycosides [2, 6]: rhaodalin (VIII) (the β-D-xylopyranoside), acetylrhodalin (IX) (the 3"-O-acetyl-β-D-xylopyranoside), diacetylrhodalin (X) (the 2",3"-di-O-acetyl-β-D-xylopyranoside), triacetylrhodalin (XI) (the 2",3",4"-tri-O-acetyl-β-D-xylopyranoside), and also myricetin 3'-O-β-D-xylopyranoside (XII) and patuloside (XIII) (luteolin 7-O-β-D-xylopyranoside [7].

Analysis of literature information shows that a definite relationship exists between the coupling constants of the vicinal protons and the conformations of sugars [8-11].

Four chair-shaped conformational formulas are possible for L-arabinosides:



In the determination of the anomeric configuration and preferred conformation of the ring, the most informative parameters are the coupling constants between the H-1 and H-2 protons, and also those between H-4 and H-5 [12]. Thus, from the PMR spectrum it is easy to distinguish the α-anomer in the C1 conformation, since only for this will an axial–axial coupling constant of the anomeric proton be realized with J = 7-8 Hz, [2, 12-15]. Conformers with diequatorial or axial–equatorial protons have a low coupling constant (0-4 Hz) of the anomeric proton [8, 13, 15], and therefore it is difficult to distinguish between them. In this case, the solution of the problem can be considerably simplified by studying the spectra of the full acetates in which the signals of the protons at C_5 can readily be seen [13, 14]. For example, small vicinal coupling constants of the two H-5 protons with the H-4 proton, indicating the equatorial orientation of the H-4 proton, permit the possibility of α- and β-anomers in the 1C conformation to be rejected and, thus, also permit an unambiguous solution of the problem in favor of the β-anomer in the C1 conformation.

Of the four chair-shaped D-xylopyranoside conformations

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TABLE 1. Chemical Shifts of the Signals of the Methylene Protons of Acetates of Flavonoid Arabinosides (I-VIII) and Xylosides (VIII-XIII) in Deuterochloroform, 100 MHz

Compound	Chemical shifts, δ, ppm		
	H-5	H-5'	$\Delta\delta_{5,5'}$
L-Arabinopyranosides			
Acetates (I)-(II)	4,20	3,60	0,60
Acetates (III)-(IV)	3,70	3,45	0,25
D-Xylopyranosides			
Acetates (VIII-XI)	4,20	3,30	0,90
Acetate XII	4,22	3,56	0,66
Acetate XIII	4,20	3,62	0,58
L-Arabinofuranosides			
Acetate V	4,19	4,03	0,16
Acetate VI	4,13	4,00	0,13
Acetate VII	4,12	3,98	0,14

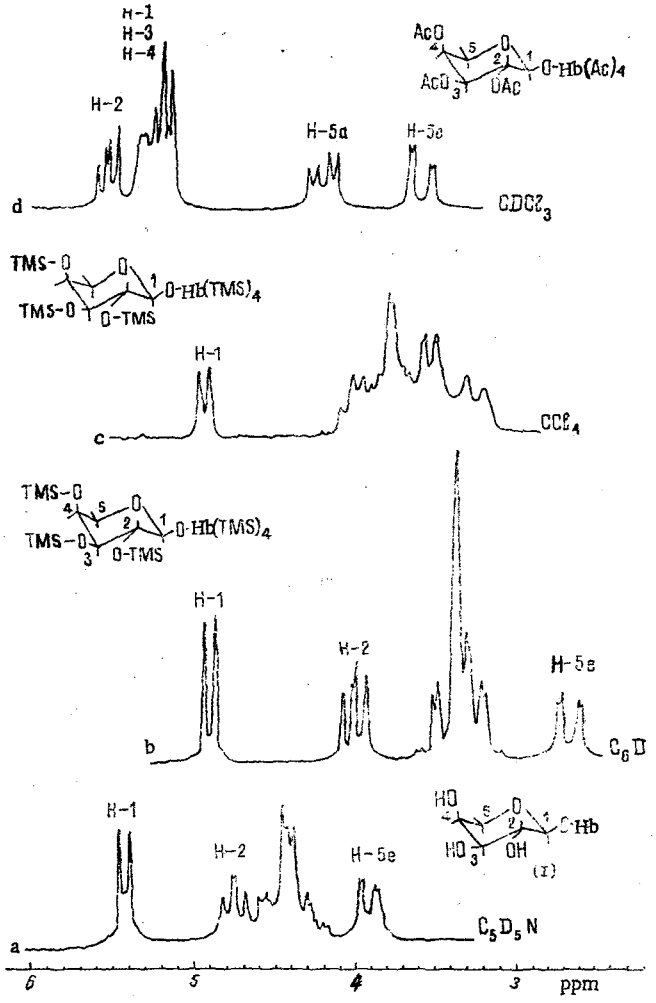


Fig. 1. Fragments of the PMR spectrum of rhodalgin (I) in deuteropyridine (a), of the TMS ether of (I) in deuterobenzene (b) and in CCl_4 (c), and of the acetate of (I) in $CDCl_3$ (d).

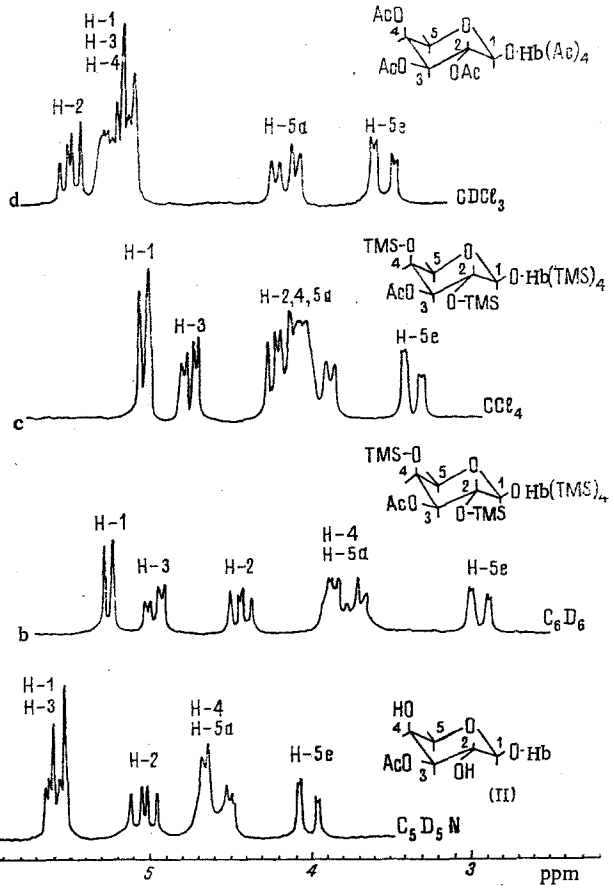
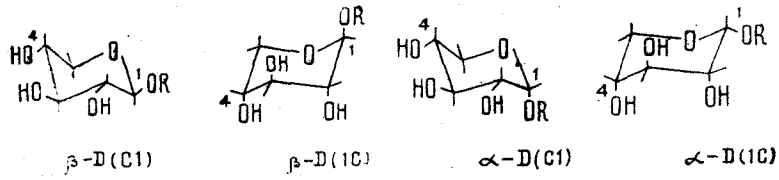


Fig. 2. Fragments of the PMR spectra of acetylrhodalgin (II) in deuteropyridine (a), of the TMS ether of (II) in deuterobenzene (b) and in CCl_4 (c), and of the acetate of (II) in $CDCl_3$ (d).



it is easy to identify the β-anomer in the C1 conformation from its PMR spectrum, which has a large coupling constant of the anomeric proton with J = 6-8, 12, 14-16 Hz; the existence of a small vicinal constant for this proton does not permit an unambiguous choice. However, a consideration of the vicinal coupling constants of the protons at C-5 with the proton at C-4 makes it possible to answer the question of the orientation of the H-4 proton and, where the constants are large, permits a choice to be made in favor of the C1 conformers which, in the case of small values of $J_{1,2}$, simultaneously corresponds to the α-anomer.

Let us consider the region of the resonance of the carbohydrate protons in the spectra of the full acetates of compounds (I-XIII) (Figs. 1-8). It is known that in the spectra of the acetoxy compounds a paramagnetic shift of the signals of the gem-acyl protons, in comparison with the hydroxy compounds, is observed, and for the methine protons this shift is greater than for the methylene protons. Consequently, in the spectra of the pentopyranoside acetates the signals of the anomeric and of the three gem-acylmethine protons should be present in the weak-field region. We do in fact observe such a pattern for the acetates of compounds (I-IV) and (VIII-XIII) (Figs. 1d, 2d, 3c, 6e, 7d, 8b, and 8d), where the signals of the carbohydrate protons form two nonoverlapping regions: the signals of the H-1, -2, -3, and -4 protons appear in a weaker field (4.9-5.9 ppm), and the signals of the methylene group are located in the 3.3-4.3 ppm region, forming a pair of quadruplets with a large chemical shift between the H-5a and H-5e signals (0.25-0.6 ppm for the arabinopyranosides and 0.58-0.9 ppm for the xylopyranosides (Table 1).

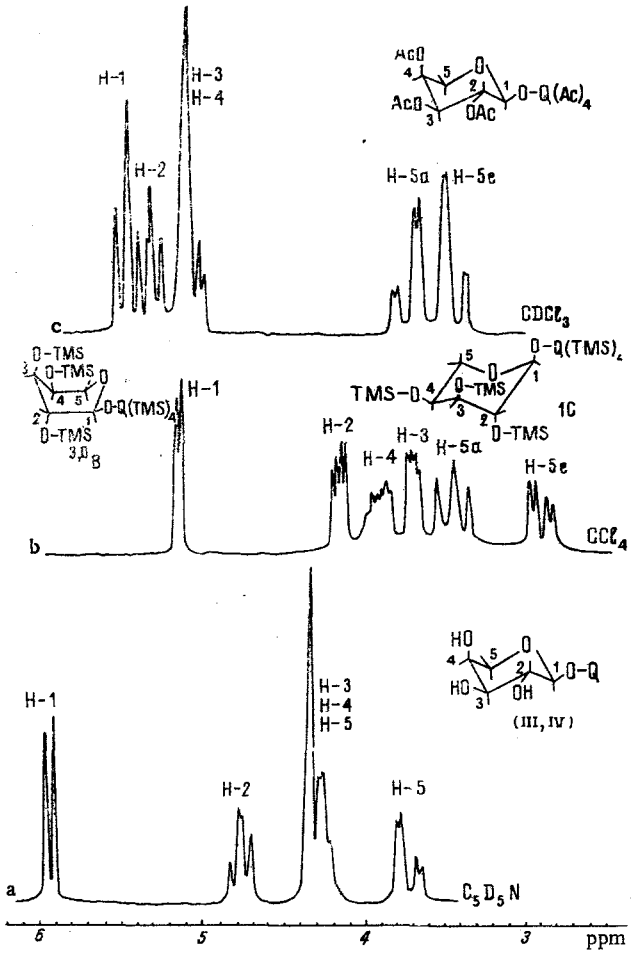


Fig. 3. Fragments of the PMR spectra of guaiaverin (III) and of polystachoside (IV) in deuteropyridine (a), of the TMS ethers of (III) and (IV) in CCl_4 (b), and of the acetates of (III) and (IV) in $CDCl_3$ (c).

The spectra of the acetates of compounds (V-VII) (Figs. 4c and 5c) are distinguished by a different arrangement of the signals: in the 4.9-5.9 ppm region there are the signals of only the three methine protons H-1, 2, 3, and in the 3.3-4.3 region appear the signals of the H-4 and two H-5 protons, the shift between the H-5 and H-5' signals amounting to not more than 0.16 ppm (Table 1). This is in harmony with the furanoid form of the arabinose in these compounds [3, 5].

Thus, in determining the size of the oxide rings of arabinose and xylose the region of the signals of the protons at C-5" and the spectra of the complete acetates (3.3-4.3 ppm) is diagnostic: for the furanosides they give two quadruplets with a large internal chemical shift, and for the furanosides the internal chemical shift of these signals is considerably smaller and the signal of the proton at C-4" accompanies them.

Furthermore, the vicinal coupling constants of the methylene protons J_{H_5,H_4} permit the arabinopyranosides ($J_{4,5a}$ = 3-4 Hz, $J_{4,5e}$ = 2 Hz) to be distinguished from the xylopyranosides ($J_{4,5e}$ = 5 Hz, $J_{4,5a}$ = 8 Hz) having the same C1 conformation.

In a study of the TMS ethers of the glycosides, it was useful to replace the traditional solvent, CCl_4, by deuterobenzene, which permitted the individual parts of the spectrum to approach a first-order spectrum (Figs. 1, 2, 6, and 7).

Let us consider the spectrum of rhodalgin ((I), Fig. 1). As has been shown above, the pyranose form of L-arabinose is shown by the multiplicity of the signals of the methylene protons (J_{gem} = 13 Hz, $J_{4,5a}$ = 4 Hz, $J_{4,5e}$ = 2 Hz) and by the large shift between the H-5a and H-5e signals in the spectrum of the acetate (Fig. 1d). The small vicinal coupling constant of the H-5 axial proton (4 Hz) shows that the H-4 proton is equatorial. In rhodalgin (Fig. 1a) and its TMS ether (Fig. 1b, c), the signal of the proton attached to the anomeric carbon atom

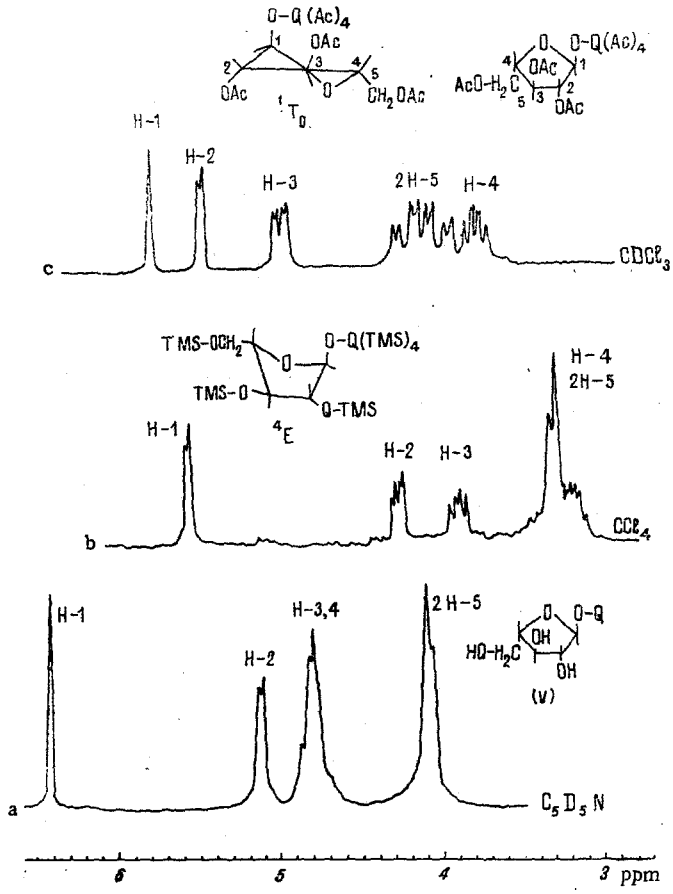


Fig. 4. Fragments of the PMR spectra of avicularin (V) in deuteropyridine (a), of the TMS ether of (V) in CCl_4 (b), and of the acetate of (V) in $CDCl_3$ (c).

H-1 is in the weakest field, forming a doublet through interaction with the H-2 proton ($J_{1,2}$ = 6 Hz). The signal of the H-2 proton can readily be seen in the spectrum of the TMS ether in deuterobenzene at 4.0 ppm. It follows from the values of its coupling constants, $J_{1,2}$ = 6 Hz and $J_{2,3}$ = 8 Hz, that the three protons H-1, H-2, and H-3 are axial. Thus, in the compound (I) investigated and its derivative the carbohydrate part is represented by α-L-arabinopyranose in the chair conformation C1.

We see a similar pattern for the derivatives of acetylrhodalgin ((II), Fig. 2). The PMR spectra of the full acetates (I) and (II) are identical. In the spectra of the TMS ether (Fig. 2b, c), distinct signals of three protons are observed in the weak field the multiplicity and coupling constants of which permit them to be assigned to H-1, H-3, and H-2, respectively. The values $J_{1,2}$ = 6 Hz, $H_{2,3}$ = 8 Hz, and $J_{3,4}$ = 3 Hz show that the H-1, H-2, and H-3 protons are axial and the H-4 proton is equatorial. For L-arabinopyranose, this corresponds to the α-anomer in the C1 conformation. The paramagnetic shift of the signal of the H-3 proton in the free glycoside and the TMS ether, as compared with rhodalgin (I), shows the attachment of the acetyl group to the 3-OH group of the arabinose in acetylrhodalgin (II).

In the study of guaiaverin (III) and of polystachoside (IV) we obtained absolutely identical spectra both for the free glycosides and for their derivatives (Fig. 3). In these compounds the arabinose has the pyranose form: this can be seen from the spectrum of the acetate, where, in the 3-4 ppm region, there are only the signals of the two geminal H-5 protons (J_{gem} = 13 Hz, $J_{4,5a}$ = 3 Hz, $J_{4,5e}$ = 2 Hz), and from the spectrum of the TMS ether, where the individual signals of all six carbohydrate protons are seen. In the free glycoside and in the acetate the anomeric H-1 proton has a coupling constant of $J_{1,2}$ = 7 Hz, which is possible for L-arabinopyranose only in the case of the α-anomer in the C1 conformation. This is confirmed by the axial orientation of the H-2 and H-3 protons ($J_{1,2}$ = 7 Hz, $J_{2,3}$ = 8 Hz, Fig. 3a) and by the equatorial orientation of the H-4 proton (small vicinal coupling constants of the two H-5 protons, Fig. 3c).

In the TMS ether (Fig. 3b), the values of the coupling constants of each of the protons at C-5 with the vicinal proton at C-4 ($J_{4,5a}$ = 9 Hz, $J_{4,5e}$ = 5 Hz) shows the axial orientation of the latter, i.e., in this compound

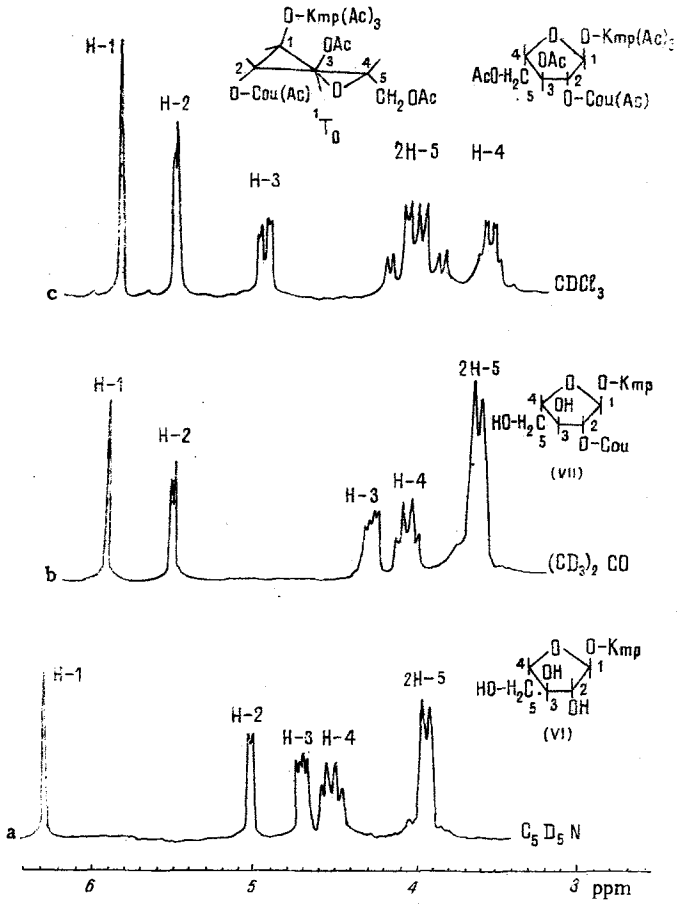


Fig. 5. Fragments of the PMR spectra of juglanin (VI) in deuteropyridine (a), of coumaroyljuglanin (VII) in deuteroacetone (b), and of the acetate of (VII) in $CDCl_3$ (c).

the arabinose adopts the 1C conformation, and this is confirmed by an analysis of the signals of the other protons ($J_{1,2}$ = 2.5, $J_{2,3}$ = 5, $J_{3,4}$ = 2.5 Hz). The coupling constant of the anomeric proton with the vicinal H-2 is 2.5 Hz, which is possible both for the α-anomer (ee) and for the β-anomer (ae). However, we excluded the β-anomer on the basis of a consideration of the spectra of the initial compound (Fig. 3a) and of the acetate (Fig. 3c). Thus, in guaiaverin and polystachoside inversion of the conformation of the pyranose ring of the arabinose takes place in the formation of the TMS ethers.

The 1C conformer of α-L-arabinopyranose has three axial substituents and in these circumstances the existence of 1,3-syn-axial coupling may impart considerable instability to the conformation. However, there is a sufficiency of examples in the literature in which the "unfavorable" conformation has proved to be the preferred one: for example, the chloride of triacetyl-β-D-xylopyranoside adopts the 1C conformation with all four substituents axial [10, p. 97]. In our case, we do not exclude the possibility of the existence of the TMS ethers of (III) and (IV) in the $^{3,O}B$ boat conformation (see Fig. 3b and the experimental part).

The investigations performed show that polystachoside cannot be an arabinofuranoside or a β-L-arabinopyranoside but is an α-L-arabinopyranoside, like guaiaverin. The inversion of the conformation observed for guaiaverin clearly shows that the established tradition of the study of the structure of flavonoid glycosides from the PMR spectra of the TMS ethers alone may lead to an inaccurate conclusion concerning structure.

In the furanosides, the methylene group is present outside the ring, and the chemical shifts of its protons are close and form a fairly narrow two-proton signal in the spectra of avicularin (V) and its TMS ether (Fig. 4a, b). On acetylation, the signals of the CH_2OAc group (Fig. 4, c) form two quadruplets (geminal constant 13 Hz and vicinal constants 4 and 5 Hz) with a chemical shift between the two H-5 signals of $\Delta\delta$ = 0.16 ppm. The signals of the gem-acyl methylene protons (2 H-5) undergo an insignificant paramagnetic shift in comparison with the signals of the gem-aceyl methine protons and are present in the 3.6-4.3 ppm region together with the

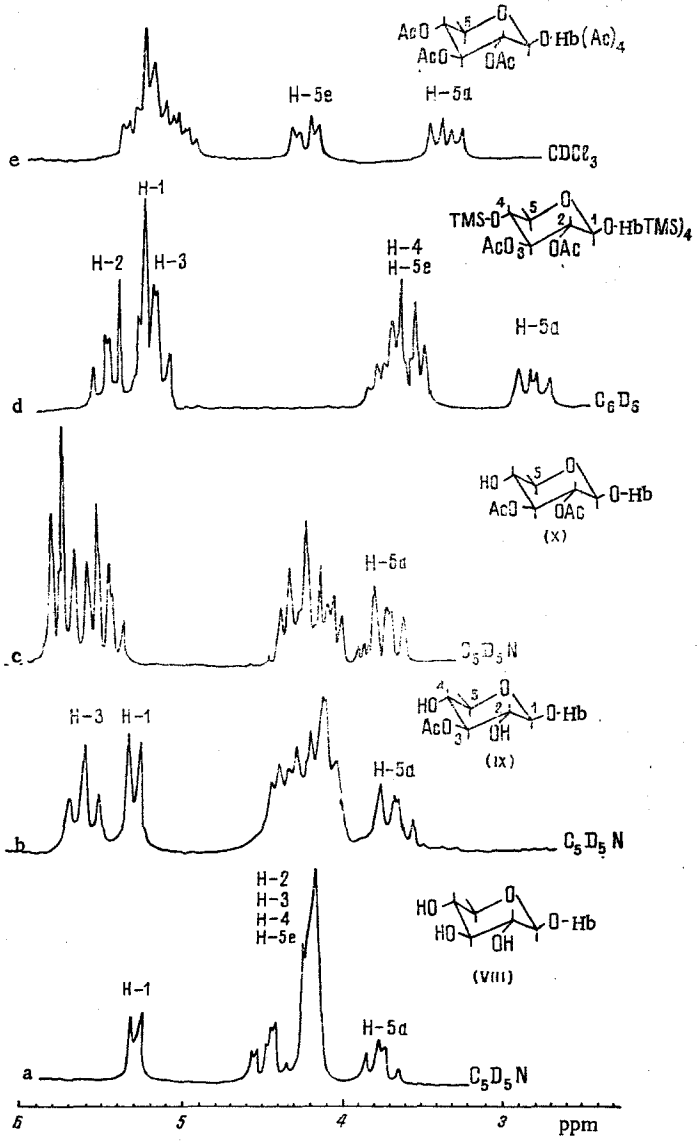


Fig. 6. Fragments of the PMR spectra of rhodalin (VIII) in deuteropyridine (a), of acetylrhodalin (IX) in deuteropyridine (b), of diacetylrhodalin (X) in deuteropyridine (c), of the TMS ether of (X) in deuterobenzene (d), and of the acetates of (VIII-X) in $CDCl_3$ (e).

H-4 signal, which permits the furanoside to be distinguished readily from the pyranoside. In the spectrum of the acetates, all the signals are well resolved and their assignment is unambiguous. A broadened H-1 singlet at 5.8 ppm agrees with literature information for 1,2-trans derivatives [8], i.e., for α-L-arabinosides. A doublet with $J = 2$ Hz corresponds to the H-2 proton, and a doublet of doublets with $J = 2$ and 5 Hz must be assigned to the H-3 proton.

The conformation of the arabinose in the molecules of avicularin and its derivatives was found in the following way. By using the values of the vicinal coupling constants in the acetate of (V) ($J_{1,2} = 0$ Hz, $J_{2,3} = 2$ Hz, $J_{3,4} = 5$ Hz) and the TMS ether of (V) ($J_{1,2} = 2$ Hz, $J_{2,3} = 4$ Hz, $J_{3,4} = 6$ Hz), we calculated the dihedral angles between the neighboring hydrogen atoms by means of the Karplus equation [17]. Then on Dreiding models we measured the dihedral angles for the 10 possible envelope (E) conformations and the 10 twist (T) conformations. The $^1T_0$ twist conformation in the acetate and the free glycoside (V) and the ^4E envelope conformation in its TMS ether showed satisfactory correlations of the projection angles with the coupling constants of the α-arabinose (see the experimental part).

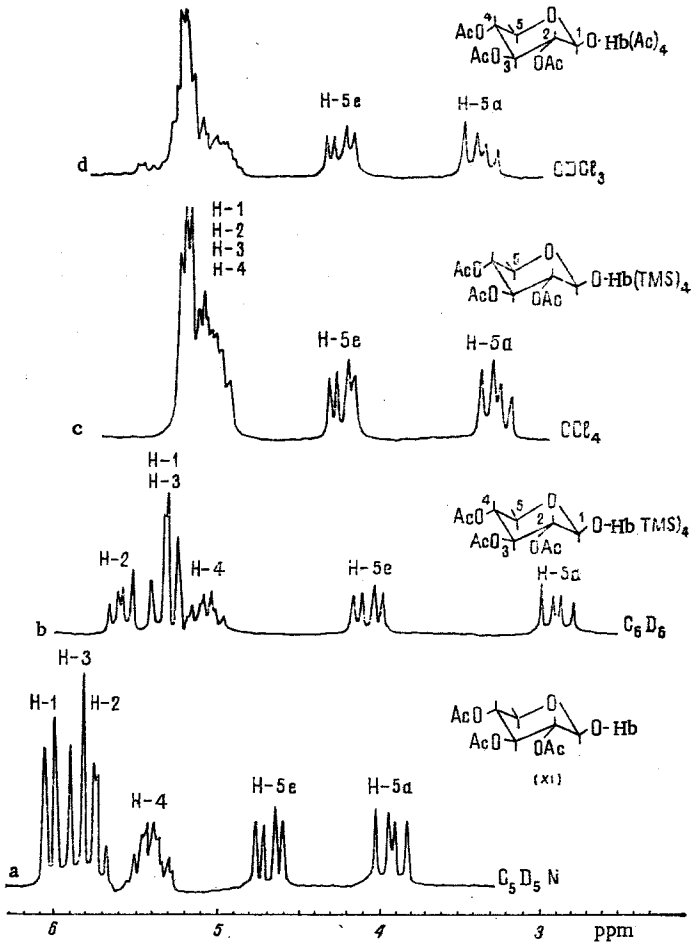


Fig. 7. Fragments of the PMR spectra of triacetylrhodalin (XI) in deuteropyridine (a), of the TMS ether of (XI) in deuterobenzene (b) and in CCl_4 (c), and of the acetate of (XI) in $CDCl_3$ (d).

The signals of the carbohydrate moiety of the juglanin molecule ((VI), Fig. 5a) scarcely differ from the analogous signals of avicularin both for the free glycoside and for the acetate. In coumaroyljuglanin ((VII), Fig. 5b), as compared with juglanin, the signal of the H-2 proton is shifted downfield, which permits the conclusion that the 2-OH group of α-L-arabinofuranose has been acylated. The values of the vicinal coupling constants ($J_{1,2} = 0$, $J_{2,3} = 2$, and $J_{3,4} = 5$ Hz) show the $^1T_0$ twist conformation in compounds (VI) and (VII) and their acetates. It must be mentioned that for methyl α-D-arabinofuranoside tribenzoate [18], which is enantiomeric in its carbohydrate moiety with the compounds (V-VII) that we have investigated, the alternative $^0T_1$ conformation has been shown, as was to be expected.

The four herbacetin xylosides studied – rhodalin (VIII), acetylrhodalin (IX), diacetylrhodalin (X), and triacetylrhodalin (XI) – give the same acetate (Figs. 6e and 7d). The nature of the signals of the methylene protons ($J_{gem} = 13$ Hz, $J_{4,5e} = 5$ Hz, $J_{4,5a} = 8$ Hz) shows the axial orientation of the H-4 proton, and the large shift between the H-5a and H-5e protons (see Table 1) shows the pyranose form of the D-xylose.

The coupling constant of the anomeric proton ($J_{1,2} = 7$ Hz) in compound (VIII) (Fig. 6a) corresponds to the β-anomer in the C1 (D) conformation.

The vicinal coupling constants $J_{1,2} = 7$ Hz, $J_{2,3} = J_{3,4} = 9.5$ Hz of the H-1 and H-3 protons in compound (IX) (Fig. 6b) also show the axial orientation of the H-1, -2, -3, and -4 protons and thereby characterize compound (IX) as the β-D-xylopyranoside in the C1 conformation. At the same time, the appearance of the signal of the H-3 proton in the weak field (δ 5.6 ppm) shows the attachment of the acetyl group to the 3-OH group of the xylose.

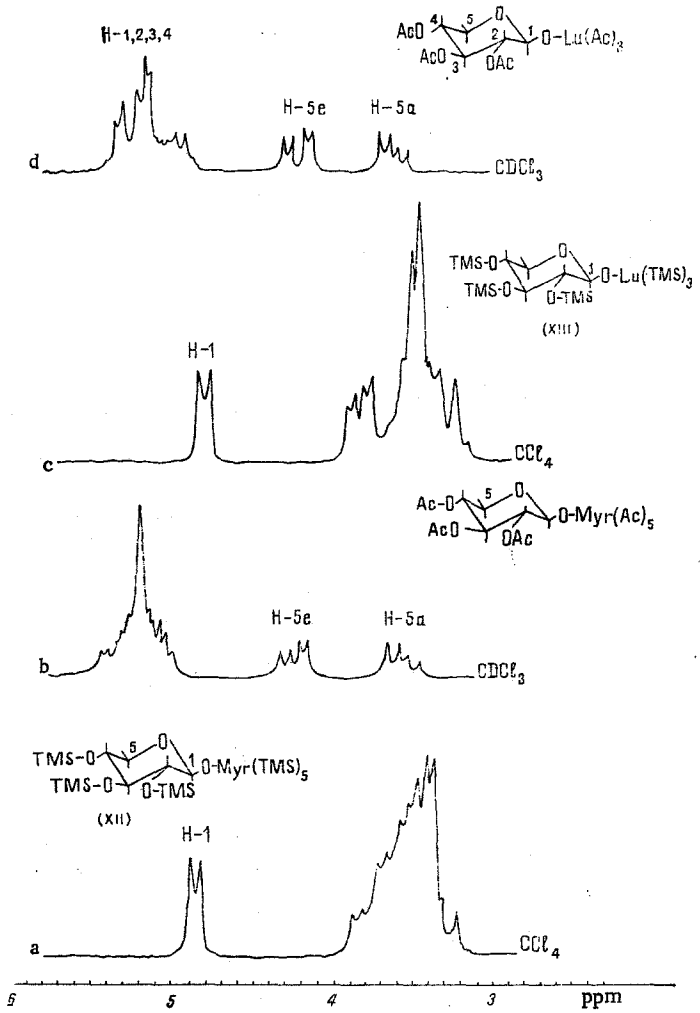


Fig. 8. Fragments of the PMR spectra of the TMS ether of myricetin xylopyranoside (XII) in CCl_4 (a), of the acetate of (XII) in $CDCl_3$ (b), of the TMS ether of patuloside (XIII) in CCl_4 (c), and of the acetate of (XIII) in $CDCl_3$ (d).

In the spectra of diacetylrhodalin ((X), Fig. 6c,d), the signals of the H-1, H-2, and H-3 protons are located in the weak field, and in the spectra of triacetylrhodalin ((XI), Fig. 7a,b), the signals of the H-1, H-2, H-3, and H-4 protons are located in the same region. This is explained by the acetylation of the 2- and 3-OH groups of the xylose in compound (X) and of the 2-, 3-, and 4-OH groups of the xylose in compound (XI). The existence of only large vicinal coupling constants shows the axial orientation of the H-1, -2, -3, and -4 protons in these compounds and also characterizes them as β-D-xylopyranosides in the C1 conformation.

The spectra of the TMS ethers of compounds (XII) and (XIII) were obtained in CCl_4 (Fig. 8a,c) and the spectra of their acetates in $CDCl_3$ in $CDCl_3$ (Fig. 8b,d). The constants of the coupling of the anomeric protons with H-2 in them show the axial orientation of the H-1 and H-2 protons, and the multiplicity of the signal of the methylene proton shows the axial nature of the H-4 proton, while the large shift between the signals of the H-5a and H-5e protons indicates the pyranose form of the xylose residue. Thus, compounds (XII) and (XIII) are likewise β-D-xylopyranosides in the C1 conformation.

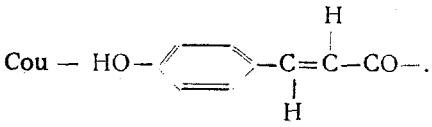
No xylofuranosides were available to us, but it may be predicted that the PMR spectra of their acetates will also contain the signals of three protons (H-4 and two H-5) in the 3.3-4.3 ppm region that have been observed for the acetates of the arabinofuranosides (V-VII).

EXPERIMENTAL

The physicochemical constants of the glycosides (I-XIII) corresponded to those given in the literature [2-7]. Generally-accepted methods were used to obtain the full acetates of the glycosides (acetic anhydride, pyridine) and the trimethylsilyl ethers (pyridine, chlorotrimethylsilane, hexamethyldisilazane).

The PMR spectra were obtained on a Varian H-100D, 100 MHz, instrument with tetramethylsilane as internal standard. The figures show fragments of the spectra that include the region of resonance of the carbohydrate protons. The following conventional symbols have been adopted:

Hb – herbacetin (3,4',5,7,8-pentahydroxyflavone),
Q – quercetin (3,3',4',5,7-pentahydroxyflavone),
Kmp – kaempferol (3,4',5,7-tetrahydroxyflavone),
Myr – myricetin (3,3',4',5,5',7-hexahydroxyflavone),
Lu – luteolin (3',4',5,7-tetrahydroxyflavone),
Ac – CH_3CO–,
TMS – $(CH_3)_3Si$–, and

Cou –  .

Using the rearranged Karplus equation [8, p. 396], from the vicinal spin–spin coupling constants we calculated the approximate values of the dihedral angles, and these were compared with the dihedral angles measured on Dreiding molecular models for the 1C chair conformation and the six theoretically possible boat conformations of α-L-arabinopyranose in the TMS ethers of (III) and (IV). A similar comparison was made for the ten twist and ten envelope conformations of the α-L-arabinofuranose residues in compounds (V-VII) and their derivatives. Table 2 gives the conformations showing satisfactory correlation of the calculated and measured dihedral angles.

A. A. Savina and V. I. Sheichenko (All-Union Scientific-Research Institute of Medicinal Plants) participated actively in the discussion of the investigation, the samples of polystachoside were provided by N. F. Komissarenko (Khar'kov Scientific-Research Institute of Pharmaceutical Chemistry), and the spectra were taken by O. G. Rud' (All-Union Scientific-Research Institute of Medicinal Plants).

SUMMARY

A comparative analysis of the PMR spectra of a number of flavonoid O-arabinosides and O-xylosides and of their full acetates and TMS ethers has been made which has permitted the determination of the conformations

TABLE 2

Compound	Vicinal coupling constant, J, Hz	Dihedral angles: calculated from Karplus equation	Dihedral angles: measured on a Dreiding model: 1C conformation	Dihedral angles: measured on a Dreiding model: $^{3,0}B$ conformation
TMS ethers of (III) and (IV)	$J_{1,2}$=2,5	$\varphi_{1,2}$=55 and 123°	60	120
	$J_{2,3}$=5	$\varphi_{2,3}$=38 and 138°	60	60
	$J_{3,4}$=2.5	$\varphi_{3,4}$=55 and 123°	60	60
	$J_{4,5}$=5	$\varphi_{4,5}$=38 and 138°	60	120
	$J_{4,5'}$=9	$\varphi_{4,5'}$=0 and 172°	180	0
			$^1T_0$ conformation	
(V), (VI), and (VII), and their acetates	$J_{1,2}$=0	$\varphi_{1,2}$=78 and 99°	100	
	$J_{2,3}$=2	$\varphi_{2,3}$=58 and 118°	120	
	$J_{3,4}$=5	$\varphi_{3,4}$=38 and 138°	140	
			^4E conformation	
TMS ether of (V)	$J_{1,2}$=2	$\varphi_{1,2}$=58 and 118°	120	
	$J_{2,3}$=4	$\varphi_{2,3}$=44 and 131°	135	
	$J_{3,4}$=6	$\varphi_{3,4}$=30 and 144°	145	

of the pentoses and of the glycosidic bonds. The region of the signals of the protons at C-5" in the spectra of the full acetates is diagnostic for determining the size of the oxide ring of a pentose residue.

Polystachoside and guaiaverin have been shown to be identical (quercetin 3-O-α-L-arabinopyranoside). Inversion of the conformation of the pyranose ring of the arabinose residue has been detected for the TMS ethers of guaiaverin and polystachoside.

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