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DETERMINATION OF THE ABSOLUTE CONFIGURATION OF CARBOHYDRATE COMPONENTS OF FLAVONOL GLYCOSIDES OF THE CHESTNUT

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As reported previously [1], from the combined flavonoids of the leaves of Aesculus hippocastanum L. (horse chestnut) we have isolated, in the individual state, four native flavonol glycosides. On the basis of a chemical and spectroscopic analysis of the glycosides, it has been established that they are 3-monosides of kaempferol and querctin, the sugar components of which are arabinose and rhamnose [2].

The present communication proves the absolute configuration of the carbohydrate residues of the glycosides studied.

It is known that glycosides, the sugar of which is present in the more highly strained furanose form, hydrolyze many times faster than glycosides in which the sugar component is present in the less strained pyranose form. Taking these facts into account, and also the capability of the glycosides mentioned for undergoing partial hydrolysis even on brief heating in neutral aqueous solution, we assumed that the furanose form of the sugar component was most probable for them.

To confirm this, we compared the time of complete acid hydrolysis of the assumed furanosides and of quercetin 3-α-L-rhamnopyranoside.

Glycosides	Time of complete hydrolysis, min
Kaempferol 3-arabinoside (SK-1)	10
Quercetin 3-arabinoside (SK-3)	10
Kaempferol 3-rhamnoside (SK-2)	34
Quercetin 3-rhamnoside (SK-4)	34
Quercetin 3-α-L-rhamnopyranoside	106

In the hydrolysis of the first four glycosides, appreciable amounts of the aglycones were formed even in the first minute, while in the case of quercetin 3-α-L-rhamnopyranoside appreciable amounts were present only in the 20-th minute.

It can be seen from an analysis of the results obtained that the rate of hydrolysis of the glycosides under our experimental conditions does not depend on the structure of the aglycones (kaempferol and quercetin) and is determined by the difference in structure of the sugar components (rhamnose and arabinose). On comparing the rates of hydrolysis of the glycosides SK-1, SK-2, SK-3, and SK-4 with the rate of hydrolysis of quercetin 3-α-L-rhamnopyranoside, it can be seen that the arabinosides hydrolyze more than ten times as fast and the rhamnosides more than three times as fast. Thus, it must be assumed that the ready hydrolyzability of the glycosides studied is due to the furanose form of the sugar component.

This is confirmed by the IR spectra of the glycosides in the 1100-900-cm^{-1} region (Table 1).

Arabinosides of kaempferol and quercetin exhibit absorption bands at 1070 and ~1046 cm^{-1}. In the rhamnosides, however, only one strong absorption band is observed at ~1062 cm^{-1}. These bands can be ascribed to the vibrations of the tetrahydrofuran ring: 1072 (very strong) and 1047 (strong) [3]. The bands mentioned above cannot relate to the absorption of a pyranose ring, since tetrahydropyran and its hydroxy derivatives [3] and, in particular, methyl α-L- and β-L-arabopyranosides [4] have four or five medium-intensity or strong bands in this region belonging both to the vibrations of the ring and to the C—O stretching vibrations in the C—OH groups.

Table 1

Frequencies of the Absorption Bands of the Carbohydrate Moieties of the Glycosides

Glycoside	Vibrations, cm^{-1}	
	Of the furanose ring	Of the terminal CH_3 groups
Kaempferol 3-arabinoside	1070, 1043	—
Quercetin 3-arabinoside	1070, 1049	—
Kaempferol 3-rhamnoside	1062	947
Quercetin 3-rhamnoside	1063	965

To determine the configuration of the glycosidic bond between the aglycones and the sugar components, we compared the molecular rotations of the glycosides investigated with those of flavonol glycosides of known structure corresponding to them (Table 2). The similarity of the values of the magnitudes being compared leads to the conclusion that the sugar components in all the glycosides are connected to the aglycones by α-glycosidic bonds and belong to the L-series. Furthermore, these data confirm once more the furanose form of the sugar components of the glycosides under study.

Table 2

Comparison of the Molecular Rotations of the Flavonol Glycosides

Glycoside	Mol. wt.	$[\alpha]_D^{22}$, deg	$[M]_D^{22}$, deg
Kaempferol 3-arabinoside	418	—166	—694
Quercetin 3-arabinoside	434	—175	—760
Kaempferol 3-rhamnoside	432	—177	—795
Quercetin 3-rhamnoside	448	—167	—748
Quercetin 3-α-L-arabofuranoside	434	—175	—760
Kaempferol 7-α-rhamnofuranoside	432	—170	—734

Experimental

Acid hydrolysis. Five small flasks were each charged with 5 ml of 96% ethanol and to each was added 15 mg of one of the glycosides mentioned previously. Then 5 ml of 0.2 M sulfuric acid was added to each and the reaction mixtures were heated at 100° C. The dynamics of the hydrolysis was checked by chromatographing samples of the hydrolysates taken at 3-minute intervals. After the chromatograms were developed in the 25% acetic acid system and then sprayed with aluminum sulfate, the spots of the initial glycosides and of the aglycones obtained were observed in UV light.

The IR spectra of the glycosides were obtained on a UR-10 spectrophotometer in the 1100-900-cm^{-1} region for the substances in the crystalline state (tablets of 2 mg of the substance in 400 mg of potassium bromide).

A polarimeter of the Schmidt-Hansts type was used to determine the optical activities of the glycosides in the form of 1% solutions in 96% ethanol.

Conclusions

On the basis of the rates of their acid hydrolysis, their optical activities, and their IR spectra, it has been established that the glycosides of Aesculus hippocastanum L. are (SK-1) 3-α-L-arabofuranosyloxy-5, 7, 4'-trihydroxyflavone, (SK-2) 3-α-L-rhamnofuranosyloxy-5, 7, 4'-trihydroxyflavone, (SK-3) 3-α-L-arabofuranosyloxy-5, 7, 3', 4'-tetrahydroxyflavone, and (SK-4) 3-α-L-rhamnofuranosyloxy-5, 7, 3', 4'-tetrahydroxyflavone.

The glycoside SK-3 is identical with avicularin isolated from the leaves of Psidium quajava [5]. The complete structures of the other three glycosides have been established for the first time.

REFERENCES

1. V. N. Spiridonov, Farmatsevtichn. zh., 3, 19-22, 1964.

2. V. N. Spiridonov, Abstracts of Papers and Communications at the IX-th Mendeleev Congress [in Russian], 4, 282-283, 1965.

3. N. Bagget, S. A. Barker, A. B. Foster, R. H. Moore, and D. H. Whiffen, J. Chem. Soc., 4565, 1960.

4. R. S. Tipson and H. S. Isbell, J. Res. NBS, 64A, no. 3, 239, 1960.

5. H. El Knaden and V. S. Mohammed, J. Chem. Soc., 3320, 1958.

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