

# A HYDROLYZABLE TANNIN SUBSTANCE FROM THE FRUIT OF

## Rosa platyacantha

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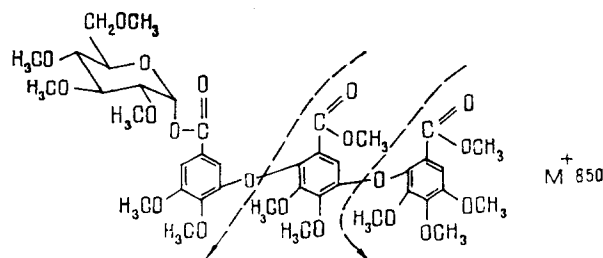
A new hydrolyzable tannin substance has been isolated from an aqueous hydrolysate of an aqueous-acetone extract of the fruit of Rosa platyacantha - 1-dehydrotri-galloyl- $\alpha$ -D-glucose - and it has been named platyacanthin. The substance is a minor component of the tannin complex.

Continuing a study of the hydrolyzable tannin substances of the flesh of the fruit of Rosa platyacantha Schrenk. [1], from the products of the stagewise water hydrolysis of the tannin complex we have isolated a substance giving a positive reaction for a pyrogallol grouping (blue coloration with trivalent iron salts). Under the action of a dilute mineral acid, the substance was hydrolyzed with the formation of glucose and of gallic, dehydrodigallic, and dehydrotrigallic acids. A negative qualitative reaction of the substance with the o-toluidine reagent indicated that the glycosidic hydroxyl of the glucose was esterified with a phenolcarboxylic acid [2].

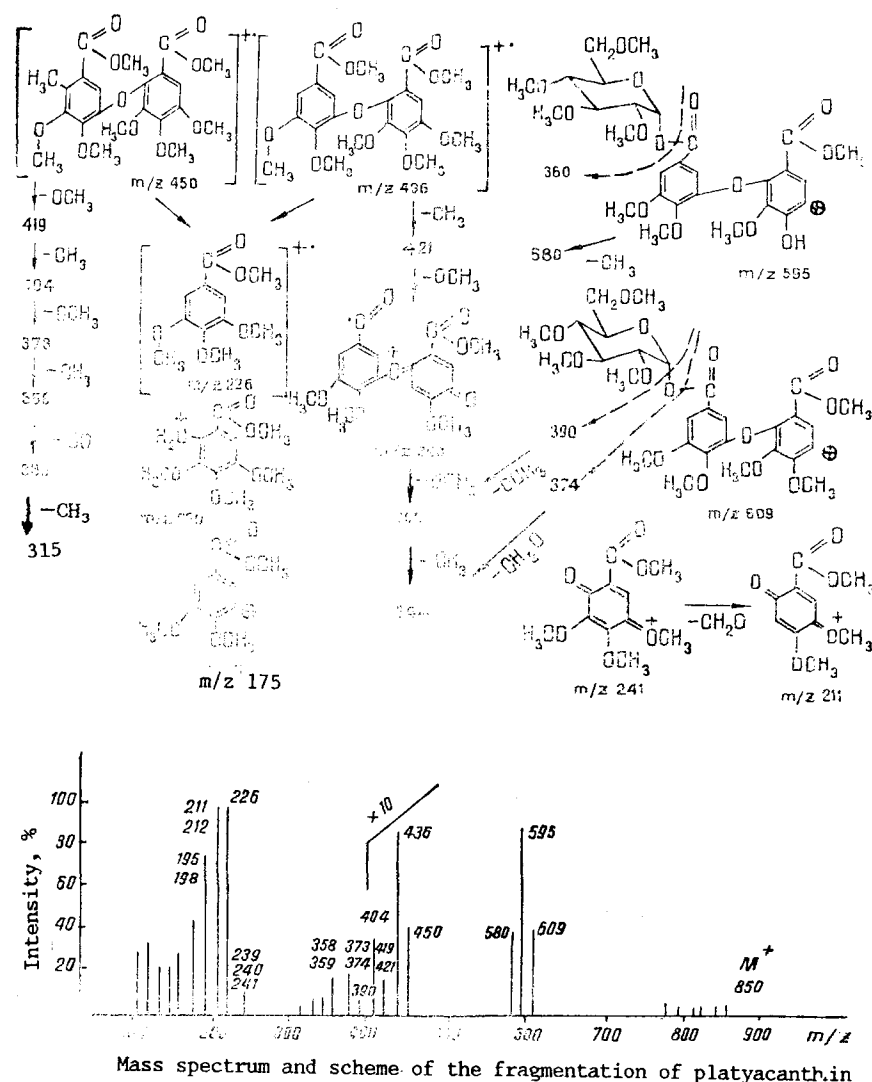
Analysis of the PMR spectrum of the peracetyl derivative permitted the conclusion that the substance was a dehydrotrigalloylglucose with the  $\alpha$  configuration of the anomeric center. The spectrum had the signals of four aromatic protons ( $\delta$ , ppm): 7.81 (s, 2H); 7.39 (s, 1 H); and 7.22 (s, 1 H), belonging, respectively, to two meta-protons of ring A and to the protons of the pentasubstituted rings B and C.

The anomeric proton of the glucose residue was recorded at ( $\delta$ , ppm) 6.2 (d, 2 Hz) and the second proton at 5.53,  $J_{H_2H_3} = 8$  Hz. In the 1.95-2.10 ppm region there were the signals of the protons of eleven acetyl groups. The presence of gallic and dehydrodigallic acids among the products of acid hydrolysis can be explained by the partial cleavage of the dehydrotrigallic acid at the ether bonds, which is in harmony with observations made previously [3].

An analysis of the mass spectrum of the permethyl derivative of the dehydrotrigalloylglucose showed that the dehydrotrigallic acid was bound to the glucose by only one ester bond and the anomeric hydroxyl was linked to the carboxy group of the tetrasubstituted benzene ring of the dehydrotrigallic acid.



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Mass spectrum and scheme of the fragmentation of platyacanthin

As can be seen from the scheme of fragmentation given the  $M^+$  850 ion corresponds to a dimethyl derivative of undecamethyldehydrotrigalloylglucose, and the ions with  $m/z$  609 and 595 are fragmentary ions formed on the cleavage at an ether bond of methyl trimethoxybenzoate without and with the migration of an alkyl group. The fragmentary ions with  $m/z$  436 and 450 correspond to the dimethyl ester of pentamethyldehydrodigallic acid cleaved at an ether bond with and without the migration of an alkyl group. Consequently, the terminal galloyl grouping of the dehydrotrigallic acid containing two aromatic protons is bound by an ester bond with the glucose [4].

On the basis of the results obtained, the structure of 1-dehydrotrigalloyl- $\alpha$ -D-glucose is proposed for the substance under investigation. No such compound has been described previously, and we have called it platyacanthin.

The substance present in an aqueous acetone extract of the flesh of the fruit of *Rosa platyacantha* in comparatively small amount and accumulates during the performance of water hydrolysis.

#### EXPERIMENTAL

The fruit of *R. platyacantha* collected in September (period of ripening) in the environs of Alma-Ata was investigated.

Chromatography was performed on Filtrak FN-11 paper in the ascending variant with the mobile phases: 1) butan-1-ol-acetic acid-water (40:12.5:29) and 2) 15% acetic acid.

The PMR spectrum was taken on a BS 487 Tesla instrument, in  $CDCl_3$  and  $(CD_3)_2CO$ , 0 - HMDS, and the mass spectrum on a Varian MAT-212 spectrometer at an ionizing energy of 70 eV

with direct introduction into the ion source.

Isolation of Platyacanthin. Since the amount of substance in the flesh was small and increased on water hydrolysis, the substance was isolated from an aqueous hydrolysate of the combined substances of the aqueous acetone extract (acetone-water (1:1)). A solution of 5 g of the dry total material in 500 ml of water was heated on the boiling water bath for 50 h. The filtrate was extracted with ether and the solution was deposited on four columns of Sephadex LH-20 (2 × 18 cm), with elution by water. The fractions giving a blue coloration with iron salts were collected in 20-ml portions and the studied by one-dimensional chromatography in solvent systems 1 and 2. The fractions containing the substance under investigation were combined and were purified on Sephadex LH-20 with water twice.

This gave 0.143 g of the substance in the form of an amorphous light brown powder readily soluble in water and aqueous acetone and insoluble in ether.  $R_f$  0.54 (system 1), 0.66 (system 2).  $[\alpha]_D^{20}$  70.7° (c 0.25; water).

The acid hydrolysis of 10 mg of the substance was performed in 1 ml of 5% hydrochloric acid at 100°C.

Acetylation was performed with acetic anhydride in pyridine at room temperature for 24 h. Light yellow crystals, mp 150-153°C  $[\alpha]_D^{20}$  159.1° (c 0.5; acetone).

Methylation was performed with an ethereal solution of diazomethane, and then with methyl iodide in the presence of silver oxide. Light yellow crystals, mp 132-134°C,  $[\alpha]_D^{20}$  25.0° (c 0.4; acetone).

#### SUMMARY

The aqueous hydrolysate of an aqueous acetone extract of the flesh of the fruit of Rosa platyacantha has yielded a new hydrolyzable tannin substance - 1-dehydrotrigalloyl- $\alpha$ -D-glucose, which has been called platyacanthin. The substance is a minor component of the tannin complex.

#### LITERATURE CITED

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