

TRITERPENE GLYCOSIDES OF HEDERA PASTUCHOVII

II. Structure Of Pastuchoside C

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A triterpene glycoside has been isolated previously from the leaves of Hedera Pastuchovii which was called "pastuchoside" C and is a monooside of hederagenin containing one molecule of rhamnose.

This paper describes the determination of the structure of pastuchoside C.

The presence in the IR spectrum of an absorption band in the 1692-cm^{-1} region (free carboxyl group), the absence of change in the glycoside when treated with ethanolic caustic potash, and the formation of the methyl ester of 23-O-methylhederagenin [2, 3] when the permethylated ether is hydrolyzed shows that the molecule of pastuchoside C has no acyl glycoside bond and also that the rhamnose is attached to the hydroxyl group of hederagenin in position 3.

For a definitive elucidation of the structure of pastuchoside C it was necessary to determine whether the rhamnose belonged to the D- or L-series, the size of the oxide ring, and the configuration of the glycoside bond. The optical rotation of the rhamnose obtained in the hydrolysis of pastuchoside C showed that it belonged to the L-series.

The stability of the glycoside to acid hydrolysis permits the conclusion that the L-rhamnose is present in the pyranose form.

The configuration of the glycoside bond and the size of the oxide ring of pastuchoside C were determined from Klyne's rule [4] by comparing the molecular rotations of the glycoside and the aglycone.

Substance	$[\text{M}]_{\text{D}}$ deg
Pastuchoside C (mol wt 618, $[\alpha]_{\text{D}} +43^{\circ}$)	+266
Hederagenin (mol wt 472 $[\alpha]_{\text{D}} +80^{\circ}$)	+378
Methyl α -L-rhamnopyranoside [5,6]	-111
Methyl β -L-rhamnopyranoside [5,6]	+170

Consequently, the L-rhamnose possesses the α -configuration for the glycoside bond and has the pyranose form for the oxide ring.

Pastuchoside C was dissolved in freshly distilled dimethylformamide and then methylated with methyl iodide in the presence of barium oxide. The results of methylation confirmed the pyranose form of the L-rhamnose, since hydrolysis of the methylated pastuchoside C yielded 2, 3, 4-trimethyl-L-rhamnose.

Thus, the results enable pastuchoside C to be characterized as O- α -L-rhamnopyranosyl-(1 \rightarrow 3)-hederagenin.

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