UDC 547.597

GLYCOSIDES OF PATRINIA INTERMEDIA

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Khimiya Prirodnykh Soedinenii, Vol. 3, No. 3, p. 217, 1967

We have previously obtained from the roots of Patrinia intermedia Roem et Schult. a triterpene glycoside, patrinoside C [1]. In addition, accompanying glycosides were found which gave no color reaction with antimony trichloride.

From a mixture containing triterpene glycosides we isolated one of them, interoside B, in the form of the acetyl derivative. For this purpose a methanolic extract of the roots of the plant was freed from reserve sugars by percolation through moist alumina, and acetylated with acetic anhydride in pyridine, and the total acetates so obtained were separated by chromatography on silica gel. In contrast to the acetates of the triterpene glycosides, the acetate of the new glycoside had a sharp melting point: 179°–180° C, $[\alpha]_D^{20}$ −76 ±8° (c 5; chloroform). Found, %: C 51.22; H 5.61. Its yield was about 1% of the methanolic extract of the roots. The cryoscopic method of determining the molecular weight gave a value of the order of 2200–2250.

In contrast to the acetate of patrinoside C, the IR spectrum of the acetate of the glycoside obtained has, in addition to the frequencies of an acetyl group at 1760 (C=O) and 1250 (C–O–C) cm^{-1}, absorption bands at 1615, 1490, 960, and 800 cm^{-1}, on the basis of which it may be assumed that the aglycone of the glycoside has an aromatic nature [2]. The hydrolysis of the acetate with mineral acid gave a crystalline aglycone with mp 78°–80° C $[\alpha]_D^{20}$ −68.5 ±3° (c 3.94; chloroform). Found: C 63.97; H 6.17. D-Glucose, mp of the osazone 205°–207° C, was identified in the filtrate by paper chromatography. The lower melting points and the percentages of carbon and hydrogen also indicated that the aglycone was not a triterpene compound.

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5 October 1966

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UDC 615.711.5

CONVERSION OF ERYSIMOSIDE INTO k-STROPHANTHIN-β

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Khimiya Prirodnykh Soedinenii, Vol. 3, No. 3, pp. 217–218, 1967

The axial hydroxyl in the digitoxose residue of erysimoside (at C-3) acetylates more slowly than all the secondary equatorial hydroxyls of the glucose residue. By making use of this property, we have synthesized k-strophanthin-β in the following way.

A solution of 2 g of erysimoside in 20 ml of pyridine was treated with 10 ml of acetic anhydride and left at 22° C for 50 min. Then the reaction mixture was diluted with 100 ml of chloroform and was neutralized in the cold with 2 N sodium carbonate solution. The chloroform layer was separated off, washed with water (4 × 15 ml), and evaporated in vacuum. The residue was transferred to a 50-ml flask, 15 g of silver oxide and 30 ml of methyl iodide were added, a glas-covered stirring rod was inserted, the flask was sealed, and methylation was carried out for 1 hr at 56° C with a magnetic stirrer switched on.

At the end of the reaction the solution was filtered, the precipitate was washed with chloroform, and the filtrate was evaporated. The residue was dissolved in 30 ml of methanol, mixed with 4 ml of methanol saturated with gaseous ammonia, and left at room temperature for 17 hr. The solution was evaporated in vacuum and the resulting mixture of cardenolides was chromatographed on 80 g of alumina with chloroform–ethanol as eluant. The eluates containing pure k-strophanthin-β were combined and evaporated and the glycoside was crystallized from water.

The k-strophanthin-β obtained in this way (0.69 g, 34%) with mp 225°–233° C $[\alpha]_D^{19}$ +32.1 ± (c 0.73; methanol) was dissolved in concentrated sulfuric acid, giving a coloration changing with time as follows: 0 min – green, 7 min – light brown, 2 hr – yellow. Enzymatic hydrolysis gave cymarin (mp 184°–187° C $[\alpha]_D^{20}$ +35.8 ±3°; c 0.61; chloroform) and D-glucose. The latter was identified by paper chromatography. A mixture of the synthesized and natural glycosides gave no depression of the melting point.

1 December 1966

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UDC 547.597+547.918

STRUCTURE OF LEONTOSIDE C

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Khimiya Prirodnykh Soedinenii, Vol. 3, No. 3, pp. 218–219, 1967

When leontoside C, a triterpene glycoside from Leontice eversmannii Bge. [1, 2] with the empirical formula $C_{47}H_{76}O_{18}$, was subjected to acid hydrolysis, hederagenin was identified as the aglycone, and of the monosaccharides D-glucose and L-arabinose were found in a ratio of 2:1.

The methylation of the glycoside with diazomethane and subsequent hydrolysis led to the methyl ester of hederagenin, which shows the presence of a free carboxy group in the trioside. The exhaustive methylation of leontoside C by Kuhn's method and acid hydrolysis of the resulting product gave the methyl ester of 23-O-methylhederagenin, 2,3,4,6-tetra-O-methyl-D-glucopyranose, and a monomethylarabinose. The latter gave a reaction with dimethylaniline trichloroacetate (violet coloration) which is characteristic for methylated aldoses with a free hydroxy group at C_4 [3]. This determines the position of one of the D-glucose molecules. In addition, the monomethylarabinose reacted with periodate reagent [4], which shows the presence in it of an α-glycol grouping and therefore the position of attachment of the second molecule of D-glucose. Consequently, the methylated arabinose that we isolated is 2-O-methylarabopyranose, and leontoside C has a branching in the carbohydrate chain, the link between the two glucose molecules and the pentose molecule being through the hydroxyls at C-3 and C-4 of the arabinose.

The undoubted genetic connection between leontosides B and C permits the assumption that in the latter the L-arabinose is attached to the aglycone by an α-glycosidic bond, and the D-glucose at C-4 by a L-arabinose-β-glycoside bond. The difference in the molecular rotations between leontosides C and B shows that D-glucose at C-3 of the arabinose is also connected by a β-glycosidic bond. Consequently, leontoside C is 4-(β-D-glucopyranosido-)-3-(β-D-glucopyranosido)-α-L-arabopyranosido-(3)-hederagenin and has the following structural formula: