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ORNITHOGALOSIDE—A NEW CARDENOLIDE GLYCOSIDE FROM THE PODS OF ORNITHOGALUM MAGNUM

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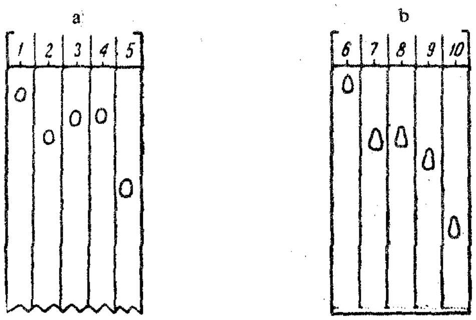
The isolation from Ornithogalum magnum Krasch et Schischk (great star-of-Bethlehem) of three substances of a cardenolide nature—A, B, and C—has been reported previously [1]. Substance A was identified as sarmentogenin 3-α-L-rhamnopyranoside (rohdexin A).

The present paper gives the results of a proof of the structure of substance B, which has been named ornithogaloside. The substance under investigation, with the empirical formula $C_{28}H_{42}O_9$, like that of rohdexin A, is not reduced by sodium borohydride, and its UV spectrum gives one maximum in the 218 mμ region (log ε 4.20) which is characteristic for a butenolide lactone ring. On acid hydrolysis, ornithogaloside is split into the aglycone ($C_{23}H_{34}O_5$), which, from its physicochemical properties, color reactions with 84% sulfuric acid and antimony trichloride, R_f values in various solvent systems, and a mixed melting point, was identified as 3β,11α,14β-trihydroxy-5β-card-20(22)-enolide (sarmentogenin), obtained from rohdexin A [1]. The sugar component of the glycoside on being treated on a chromatogram with aniline phthalate [2], appears in the form of a red spot at the level of L-arabinose (figure, a, samples 3 and 4) and gives no depression of the melting point with an authentic sample of L-arabinose, and its phenylosazone has R_f values (figure, b, samples 7 and 8) and physicochemical properties identical with those of the phenylosazone of L-arabinose.



Paper chromatograms in the 1-butanol—acetic acid—water (4 : :1 : 2) system; 48 hr, 20° C (a); and in the chloroform—formamide system, 1 hr 30 min, 23° C, GOZNAK paper (b): 1) D-glucose; 2) D-xylose; 3) sugar component of ornithogaloside; 4) L-arabinose; 5) L-rhamnose; 6) phenylosazone of D-glucose; 7) phenylosazone of the sugar component of ornithogaloside; 8) phenylosazone of L-arabinose; 9) phenylosazone of D-xylose; 10) phenylosazone of L-rhamnose.

Using Klyne's rule [3], the glycoside was found to contain an α-glycosidic bond. The difficulty of acid hydrolysis shows the presence of the pyranose form [4, 5] of the carbohydrate part of the substance studied.

Thus, the structure of ornithogaloside can be given as 3β-(O-α-L-arabinopyranosyl)-11α,14β-dihydroxy-5β-card-20(22)-enolide.

The presence of L-arabinose as the sugar component of cardiac glycosides is an extremely rare phenomenon.

Experimental

The melting points were determined on a Kofler apparatus. For analysis, the substances were dried in vacuum (10^{-2} mm Hg) over P_2O_5 at 110–115° C for 5 hr.

Ornithogaloside (substance B). The method of isolating the substance under investigation was described in the previous communication [1]. The glycoside was crystallized from acetone—water with subsequent recrystallization from methanol (after evaporation), mp 227–234° C, $[\alpha]_D^{23}$ 0 ± 2° (c 1.0; methanol). Found, %: C 64.37; 64.30; H 8.03; 8.14. Calculated for $C_{28}H_{42}O_9$, %: C 64.33; H 8.09.

The substance gives the Legal and Raymond reactions characteristic for cardiac glycosides with five-membered unsaturated lactone rings [6]. With 84% sulfuric acid it forms colorations changing with time: 0 min—colorless, rapidly changing to reddish; 5–10 min—brown; 15–20 min—brown with a deep blue border; 25–40 min—blue-brown; 45–70 min—green-blue; 80–105 min—blue-green; 120 min—bright green.

Acid hydrolysis of ornithogaloside. A solution of 90 mg of the glycoside in 10 ml of anhydrous acetone was treated with 0.1 ml of concentrated hydrochloric acid and left at room temperature. The degree of hydrolysis was followed by means of paper chromatography in the chloroform—formamide system. On the 7th day, the initial substance was completely absent from the hydrolysate. The further treatment was performed by the usual method [7]. The sugar component and the aglycone were obtained by the procedure described previously [7].

Aglycone of ornithogaloside. The color reactions with sulfuric acid and antimony trichloride, paper chromatography in the chloroform—formamide, methyl ethyl ketone—xylene (1 :1)/formamide, and isoamyl alcohol—water (1 :1) systems, and also a mixed melting point showed that the aglycone was identical with sarmentogenin [1].

Sugar component of ornithogaloside. After recrystallization from ethanol—ether, 12 mg of a sugar with mp 160–161° C was obtained. Paper chromatography in the 1-butanol—acetic acid—water (4 :1 :2) and 1-butanol—pyridine—water (6 :4 :3) systems and a mixed melting point confirmed the identity of the sugar residue of the glycoside as L-arabinose.

Phenylosazone of the sugar component of ornithogaloside. The substance was obtained as described by Kiliani [8], mp 163–164° C. A mixture with an authentic sample of the phenylosazone of L-arabinose gave no depression of the melting point. On paper chromatography (figure, b, samples 7 and 8), the phenylosazones of the sugar residue of ornithogaloside and of L-arabinose had the same R_f values. The spots of the phenylosazones on the chromatogram were revealed in UV light; they fluoresced yellowish blue.

Conclusions

From the pods of Ornithogalum magnum Krasch et Schischk. has been isolated a cardenolide glycoside which has been given the name ornithogaloside; its structure can be given as 3β-(O-α-L-arabinopyranosyl)-11α, 14β-dihydroxy-5β-card-20(22)-enolide.

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