CARDENOLIDES OF THE SEEDS OF Ornithogalum magnum

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The isolation of several cardenolide glycosides from the seed pods of Ornithogalum magnum Krasch. et Schischk., family Liliaceae, has been reported previously [1]. The present paper gives the results of a study of the cardenolides of the seeds of this plant.

To isolate the group of substances to be investigated, the comminuted seeds, after being defatted with petroleum ether, were extracted with ethanol. The extract was evaporated to eliminate the solvent, the residue was dissolved in water, and the solution was treated with chloroform and with mixtures of chloroform and alcohol (4:1 and 2:1) [2]. After the solvent had been distilled off, the glycosides of the fractions were separated by partition chromatography on silica gel or by adsorption chromatography on alumina [1]. Five substances of cardenolide nature were obtained.

Rhodexin B, $C_{29}H_{44}O_9$, mp 248-253°C, $[\alpha]_D^{22}-30°$ (c 0.1; ethanol). After the substance had been treated with 85% phosphoric acid [3], a bright blue fluorescence in UV light was observed, which showed the presence of a hydroxyl, an acyl residue, or a double bond at C_{16} of the steroid skeleton. The products of acid hydrolysis [4] were found to contain L-rhamnose and the aglycone gitoxigenin, with the products of its degradation (16-anhydrogitoxigenin and 14,16-dianhydrogitoxigenin). The stability of the glycoside to acid hydrolysis with 0.05 N sulfuric acid gave grounds for stating that the L-rhamnose in the substance under investigation is present in the pyranose form. An α-glycosidic linkage in the glycoside was established by Klyne's method [5]. The facts given show that we had obtained rhodexin B. A similar compound has been isolated by Japanese workers from Rhodea japonica (Thunb.) Roth. [6].

Rhodexin A, $C_{29}H_{44}O_9$, mp 249-252°C, $[\alpha]_D^{21}-23°$ (c 0.1; ethanol). We have obtained this glycoside previously from the seed pods of the same plant [1].

Rhodexoside, $C_{35}H_{54}O_{14}$, mp 179-182°C, $[\alpha]_D^{20}-24°$ (c 0.1; ethanol). The glycoside was cleaved by the enzymes of the grape snail into rhodexin A and D-glucose, which is attached to the monoside by a β-glycosidic linkage. The capacity of the initial substance for forming an acetonide [7, 8] shows the attachment of the D-glucose to the L-rhamnose by a 1→4 bond. These properties correspond to rhodexoside, which has been found previously in O. umbellatum L. [9].

Substance C, according to preliminary results has the general formula $C_{29}H_{44}O_{10}$, mp 250-254°C, $[\alpha]_D^{19}-20.8°$ (c 2.4; methanol). Acetate of substance C, $C_{39}H_{54}O_{15}$, mp 156-160°C, $[\alpha]_D^{19}-16.7°$ (c 1.0; methanol); 28.3% of acetyl groups, corresponding to five acetyl residues. The substance does not fluoresce with 85% phosphoric acid in UV light. With 84% sulfuric acid it gives a coloration changing with time: 0 min – colorless; 1 min – brownish yellow; 5-40 min – brown; 50-120 min – cherry-red with a brown tinge; 125-140 min – violet with a brown tinge. On hydrolysis [4], the glycoside split into a methylpentose, which in a number of systems [10] had the same R_f value as D-gulomethylose [2], and an aglycone, which was obtained in the amorphous state. Its acetate melted at 155-159°C, $[\alpha]_D^{22}+11°$ (c 0.1; ethanol).

Substance D, $C_{35}H_{54}O_{15}$, mp 246-251°C, $[\alpha]_D^{20}-14°$ (c 0.1; ethanol) is a bioside and is cleaved by snail enzymes into substance C and D-glucose. With 84% sulfuric acid substance D forms colorations changing with time similar to those described for substance C.

Substances C and D have also been isolated from the seed pods and bulbs of O. magnum.

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LITERATURE CITED

1. N. F. Komissarenko, Khim. Prirodn. Soedin., 156 (1965); 46 (1969); 38 (1971).
2. N. F. Komissarenko, V. T. Chernobai, and D. G. Kolesnikov, Med. Prom. SSSR, 1961, No. 1, 12.
3. P. Bellet, Ann. Pharmac. Franc., 8, 471 (1950).
4. C. Mannich and G. Siewert, Chem. Ber., 75, 737 (1942).
5. W. Klyne, Biochem. J., 47, No. 4, xli (1950).
6. H. Nawa, J. Pharm. Soc. Japan, 72, 404 (1952).
7. I. F. Makarevich, Khim. Prirodn. Soedin., 267 (1969).
8. H. Kubinyi, W. Staidle, and B. Görlich, Arch. Pharm., 304, 380 (1971).
9. J. A. Smith and G. R. Paterson, J. Pharm. Pharmacol., 19, 221 (1967).
10. M. T. Krauss, H. Jäger, O. Schindler, and T. Reichstein, J. Chromatog., 3, 63 (1960).