ADONIS GLYCOSIDES

II. THE STRUCTURE OF SUGOROSIDE

R. Sh. Yamatova, V. A. Maslennikova,
R. Z. Aitova, and N. K. Abubakirov

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Continuing a study of the cardenolides of *Adonis chrysocyathus* Hook, f. et Thom. (local name "sugur-ut" – "marmot grass") we have found in this plant, in addition to cymarin and k-strophanthin-β [1], yet another glycoside with mp 202-204°C, $[\alpha]_D^{24}$ +16.4± 2° (c 2.05; chloroform), which we have called sugoroside.

The glycoside gives a positive Keller–Kiliani reaction and a positive reaction with xanthydrol. Complete acid hydrolysis of the compound led to strophanthidin, $C_{23}H_{32}O_6 \cdot H_2O$ with mp 176-178°C, $[\alpha]_D^{22}$ +43.8° (c 2.03; methanol). A spectrometric determination of the molecular weight of sugoroside at 218 nm in comparison with strophanthidin [2] gave: 995.4, 1012.5. Calculated for $C_{50}H_{78}O_{20}$, mol. wt. 999.2. Analysis showed the presence of three methoxy groups in the substance (calculated to the given formula).

The results of gas-liquid chromatography [3] showed that the glycoside contained one molecule of D-glucose, two molecules of D-cymarose, and another sugar the nature of which could not be immediately determined.

Sugoroside was hydrolyzed with 0.1% HCl in dioxane (98°C, 1 h). Preparative separation of the sugar fraction of the hydrolyzate in a thin layer of silica gel gave D-cymarose and, in the form of a syrup, an unknown disaccharide. Subsequent hydrolysis of the disaccharide in 5% sulfuric acid gave D-glucose and D-diginose. The enzymatic cleavage of sugoroside with the pancreatic juice of the snail *Helix plectotropis* (38.7°C, one day) led to the splitting out of D-glucose. When the resulting desglucosugoroside was hydrolyzed with 0.1% HCl in dioxane, D-cymarose and D-diginose were obtained. Consequently, the D-glucose occupies the terminal position in the sugar chain and in the glycoside itself is directly attached to the D-diginose.

When sugoroside was hydrolyzed with 0.1 N H_2SO_4 in a thermostat (38°C, 20 h), among the other decomposition products we found cymarin $C_{30}H_{44}O_9 \cdot CH_3OH$, mp 144°C, $[\alpha]_D^{24}$ +36.8° (c 1.40; ethanol).

The formation of cymarin confirms that D-cymarose is attached directly to the aglycone. The other molecule of cymarose apparently connects the cymarin to the diginose. As a working formula, we ascribed to sugoroside the structure of D-glucosyl-(1 → 4)-D-diginosyl-(1 → 4)-D-cymarosyl-(1 → 4)-D-cymarosyl-(1 → 3')-strophanthidin.

The reduction of sugoroside with sodium tetrahydroborate gave sugorosol with mp 215-216°C, $[\alpha]_D^{24}$ +17.3 ± 2° (c 1.61; chloroform). Found: mol. wt. 997.8 (spectrophotometrically at 218 nm). $C_{50}H_{80}O_{20}$. Calculated: mol. wt. 1001.2. The hydrolysis of sugorosol with 0.1 N H_2SO_4 gave strophanthidol, $C_{23}H_{34}O_6$, with mp 142-145°C, $[\alpha]_D^{24}$ +47.2° (c 1.25; methanol) and the same sugars as in the cleavage of sugoroside.

LITERATURE CITED

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