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CARDENOLIDE GLYCOSIDES OF *Cheiranthus allioni*. XV. GLUCOCHEIRANTHOSIDE

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Another new cardenolide glycoside has been isolated from the plant Cheiranthus allioni *Hort., and has been named glucocheiranthoside. Its chemical structure has been established as 3β-(4'-O-β-D-glucopyranosyl-β-D-gulomethylpyranosyloxy)-14-hydroxy-19-oxo-5β,14β-card-20(22)-enolide.*

As already reported, 34 native cardenolides have been isolated from the seeds of *Cheiranthus allioni* Hort. Continuing the investigation of this plant, we have isolated another new cardenolide glycoside, which, after its chemical structure had been established, was given the name glucocheiranthoside (**1**).

The glycoside was obtained by preparative column chromatography on cellulose from the so-called medium-polarity glycoside fraction. From this fraction we also isolated two glycosides known for this plant — erysimoside and erycoridin.

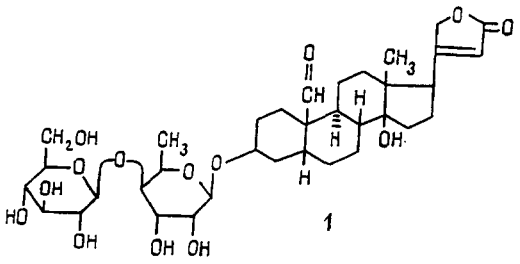
Glucopyranoside (**1**) has the composition $C_{35}H_{52}O_{14}$. Its molecule contains an aldehyde group, the presence of which was characterized both by chemical transformations and by the IR spectrum, which contained well-defined bands at 2760 and 1720 cm^{-1}. On oxidation with potassium permanganate, compound (**1**) formed a carboxylic acid.

Under the action of an enzyme preparation obtained from the pancreatic juice of the grape snail, the diglycoside (**1**) was hydrolyzed with the formation of a monoglycoside and a monosaccharide, which were isolated in the individual state and from their properties and also from the results of a direct comparison with authentic samples, were identified as cheiranthoside and D-glucose. Cheiranthoside is 3β-(β-D-gulomethylopyranosyloxy)-14-hydroxy-19-oxo-5β,14β-card-20(22)-enolide [2].

Taking these facts into account, it was then necessary to establish the site of attachment of the D-glucose in (**1**), the configuration of the glucosidic bond, and the size of the oxide ring. In order to obtain answers to these questions, we carried out the following transformations of glycoside (**1**).

In view of the comparative ease of the acid hydrolysis of glycosides containing D-gulomethylose, we performed a controlled process under mild conditions with the aim of isolating a disaccharide. As a result, we obtained an aglycon, which was identified as cannogenin, and a mixture of sugars consisting of D-glucose and a disaccharide in a ratio of 1:4. The disaccharide was obtained in the individual state with the aid of preparative paper chromatography, and from its properties and also as the result of direct comparison with an authentic sample it was identified as erycordinobiose. As is known [3], erycordinobiose is 4-O-β-D-glucopyranosyl-D-gulomethylose.

The formation from (**1**) of the aglycon cannogenin, the monoglycoside cheiranthoside, and erycordinobiose of known structure enables us to represent the structure of the new glycoside unabiguously in the following way: 3β-(4'-O-β-D-glucopyranosyl-β-D-gulomethylpyranosyloxy)-14-hydroxy-19-oxo-5β,14β-card-20(22)-enolide (**1**). An additional confirmation of the correctness of the structure given was the conversion of (**1**) into the known glycoside erycordin [4] by its reduction with sodium tetrahydroborate. In accordance with its structure, the trivial name glucocheiranthoside is proposed for the new glycoside (**1**).



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EXPERIMENTAL

The elemental analyses of the substances were carried out with the aid of an automatic C–H–N analyzer: the results of the analyses corresponded to the calculated figures. Melting points were determined on a Kofler block. Paper chromatography was conducted with the following solvent systems: toluene-butan-1-ol (1:1)/water, chloroform–tetrahydrofuran (1:1)/formamide, and butan-1-ol–acetic acid–water (4:1:2).

The isolation of the glycosides was achieved from the "medium-polarity" fraction obtained previously [6] by its chromatography on a column of powdered cellulose. The ratio of the total substances to be separated and the cellulose was 1:200. The eluent was toluene–butan-1-ol (2:1 and 1:1)/water.

Glucocheiranthoside (1), $C_{35}H_{52}O_{14}$, mp 148-152°C (methanol–isopropanol), $[\alpha]_D^{20}$ −44.4 ± 3° (*c* 0.70; methanol).

Erycordin, $C_5H_{54}O_{14}$, mp 201-213°C (ethanol), $[\alpha]_D^{20}$ −25.1 ± 3° (*c* 0.45; methanol).

Erimoside, $C_{35}H_{52}O_{14}$, mp 171-173°C (isopropanol), $[\alpha]_D^{20}$ +19.0 ± 3° (*c* 0.45; methanol).

The enzymatic hydrolysis of glycoside (1) and the working up of the hydrolysate were carried out as described in [5]. As a result, a monoglycoside with mp 154-156°C, $[\alpha]_D^{20}$ −41.1 ± 3° (*c* 0.40; methanol) and a monosaccharide with mp 145-146°C were obtained. A direct comparison with authentic samples by mixed melting points and by paper chromatography showed the identity of the compounds as cheiranthoside and D-glucose, respectively.

Partial Acid Hydrolysis of Glycoside (1). A mixture of a solution of 0.12 g of glycoside (1) in 1 ml of ethanol and 1 ml of 0.1 N H_2SO_4 and was fused into a glass tube and heated at 60°C for 16 h. The hydrolysate was treated with sodium/barium carbonate, and the precipitate was separated off. The aglycon was extracted from the filtrate with chloroform and was crystallized from water. The aglycon obtained had mp 202-210°C $[\alpha]_D^{20}$ −15.0 ± 3° (*c* 0.30; chloroform); it was identical with a sample of cannogenin both in its properties and according the results of a direct comparison.

The aqueous phase, which, according to chromatographic analysis, contained D-glucose, erycordinobiose, and the initial glycoside (1), was concentrated, and the crystals of the glycoside (1) that had deposited were filtered off. The mixture of sugars was separated by preparative paper chromatography in the solvent system butan-1-ol—acetic acid—water (4:1:2). The disaccharide was crystallized from ethanol; mp 133/160-163°C, identical with a sample of erycordinobiose.

Reduction of Glycoside (1). Over 20 min, 15 mg of sodium tetrahydroborate was added in small portions to a solution of 50 mg of glycoside (1) and 50 mg of mannitol in 5 ml of 80% dioxane. Then 5 ml of 5% sulfuric acid was added to the reaction mixture. The reduced glycoside was extracted with a mixture of chloroform and ethanol (2:1) (3 × 30 ml). The combined chloroform–ethanolic solution was washed with water (2 × 5 ml) and evaporated. The product was crystallized from ethanol, and then had mp 200-203°C. A mixed melting point with an authentic sample and a chromatographic comparison showed its identity as erycordin.

REFERENCES

1. I. F. Makarevich, Khim. Prir. Soedin., 305 (1992).
2. I. F. Makarevich, Khim. Prir. Soedin., 331 (1970).
3. I. F. Makarevich, Khim. Prir. Soedin., 50, (1973).
4. I. F. Makarevich, M. Ya. Tropp, and D. G. Kolesnikov, Dokl. Akad. Nauk SSSR, No. 4, 147, 849 (1962).
5. I. F. Makarevich, K. V. Zhernoklev, and T. V. Slyusarskaya, Khim. Prir. Soedin., 693 (1991)
6. I. F. Makarevich, Khim. Prir. Soedin., 566 (1970).