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# CARDIAC GLYCOSIDES OF *Erysimum contractum*
# III. GLUCOCANESCEIN

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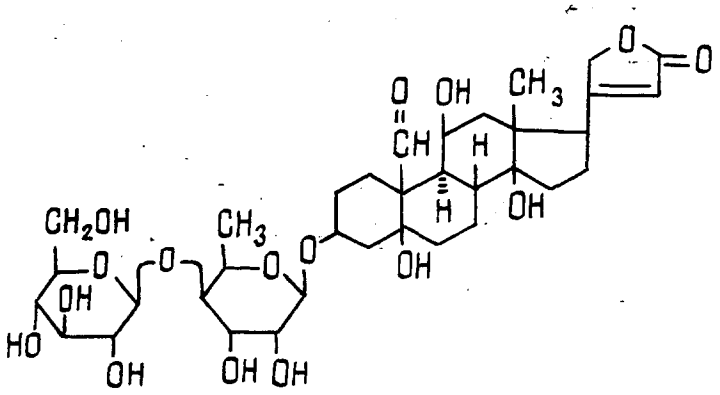
As already reported [1, 2] a number of cardenolides, including some new ones, have been isolated from the seeds of *Erysimum contractum* Somm. et Lev. Continuing an investigation of this plant, we have isolated another polar cardenolide — a glycoside which is one of the main components of the glycoside mixture. The separation of the polar compounds was achieved with the aid of preparative column chromatography on cellulose using the solvent system toluene–butan-1-ol (1:2)/water. The chromatographically individual glycoside obtained had mp 245-248°C (butan-1-ol), $[\alpha]_D^{20}$ — 26.1 ± 3° (c 0.5; ethanol). Its elementary analysis corresponded to the composition of a diglycoside, $C_{35}H_{52}O_{16}$.

The enzymatic hydrolysis of the diglycoside and the usual working up procedure permited the isolation of a monoglycoside having mp 193-195°C ($H_2O$), $[\alpha]_D^{20}$ — 23.3 ± 3° (c 0.3; ethanol). From its properties and the results of a direct comparison with a specimen, the monoglycoside was identified as canescein [3]. D-Glucose was identified chromatographically in the hydrolysate.

The experimental facts presented show that the polar glycoside isolated from the plant was a glucocanescein. A glucocanescein has been isolated previously from *Erysimum canescens* Roth by Lyu Yun-lun et al. [4, 5], but its chemical structure and also the structure of the monoglycoside monoglycoside were shown incompletely and erroneously. We have investigated canescein, nd its structure in corrected form is that of nigrescigenin 3β-O-β-D-gulomethylopyranoside [3].

In view of the investigations of the canescein monoglycoside that we had performed previously [3], it was necessary to establish for the diglycoside glucocanescein the size of the oxide ring of the D-glucose unit, the configuration of the glycosidic bond, and the position of attachment of the D-glucose residue. With this aim, we performed a controlled acid hydrolysis of glucocanescein under mild conditions (0.05 N $H_2SO_4$, 60°C, 16 h). After the usual working up, the hydrolysate contained a mixture of D-glucose and a disaccharide in a ratio of 1:4. With the aid of preparative chromatography on paper the disaccharide was obtained in the individual state, and it was identified by its mp of 133-136°C (ethanol)and by a direct comparison with an authentic sample as erycordinobiose. As is known [6], erycordinobiose is β-D-glucopyranosyl-(1→4)-D-gulomethylose. The formation of erycordinobiose from glucocanescein gives the answers to the questions posed above.

Thus, glucocanescein may be unambiguously characterized as 3β-(4′-O-β-D-glucopyranosyl-β-D-gulomethylopyranosyloxy)-5,11α,14-trihydroxy-19-oxo-5β, 14β-card-20(22)-enolide and the structure be represented by the formula (given in corrected, refined, form for the first time)

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