

ERYSIMUM GLYCOSIDES

VII. CARDENOLIDES OF *Erysimum altaicum*

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As we have reported previously [1] an ethanolic extract of the epigeal part of the plant *E. altaicum* C. A. M. contains eight substances, which have been called provisionally in the order of increasing polarity glycosides A, B, C, D, E, F, G, and H. To separate them we have used partition chromatography on a column of alumina. Elution was performed with the water-saturated toluene-butanol (1:1) system. Erysimin (glycoside A), erysimoside (glycoside D) and three other compounds have been isolated in the individual state.

Desglucocheirotoxin (glycoside B), $C_{29}H_{42}O_{10}$, was obtained in the amorphous form after the preparative separation of the fractions containing this glycoside on chromatographic cardboard in the chloroform-isoamyl alcohol (1:1)-water system. Glycoside B was identified chromatographically in several systems with an authentic sample of desglucocheirotoxin isolated from *Cheiranthus cheiri* [2].

Glycoside C formed an amorphous powder with $[\alpha]_D^{20} -19 \pm 3^\circ$ (c 1.94; methanol). Color reaction with conc. sulfuric acid in time: 0 min - lemon yellow, 5 min - orange, 10 min - orange with pink edges, 25 min - red-violet, and 45 min - violet. $\lambda_{max}^{C_2H_5OH}$ 220 nm (butenolide ring); ν_{max}^{KBr} : 3400 (OH), 1720, 1630 cm^{-1} (butenolide ring). The UV spectrum lacks the absorption band corresponding to an aldehyde group. The Mannich hydrolysis of the glycoside [3] led to the formation of a mixture of three substances the structures of which could not be established. The sugar component was identified as D-gulomethylose by paper chromatography in the butanol-methyl ethyl ketone-borate buffer (1:1:2) system, and also by gas-liquid chromatography.

Erydiffuside (glycoside E), $C_{29}H_{42}O_{11}$, mp 192-194°C (from ethanol), $[\alpha]_D^{20} -15.2^\circ$ (c 1.97; methanol) dissolved in conc. sulfuric acid, giving a yellow-brown coloration changing after an hour to a somewhat dirty green. The acid hydrolysis of glycoside E by Mannich's method [3] gave a mixture of aglycones and a carbohydrate fraction. The mixture, consisting of four substances, was separated preparatively in a fixed layer of silica gel in the benzene-chloroform-methanol (5:5:2) system. The main product proved to be an anhydro compound with mp 256-260°C (from acetone), which dissolved in conc. sulfuric acid forming a red-brown coloration changing to yellow after 40 min.

The mass spectrum of the anhydroaglycone (180°C, 40 V) had, in addition to the molecular ion with M^+ 402, peaks with m/e 384 ($M - H_2O$), 366 ($M - 2H_2O$), 356 ($M - H_2O - CO$), 348 ($M - 3H_2O$), 338 (356-18). These peaks indicate that the aglycone contains four hydroxy groups. In addition, the fragment with m/e 356 confirms the presence of an angular aldehyde group at C₁₀.

The presence of D-gulomethylose in the carbohydrate fraction of erydiffuside was confirmed by gas-liquid chromatography.

LITERATURE CITED

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