was eluted with distilled water at the rate of 90 ml/hr. Each fraction (10 ml) was analyzed qualitatively by thin-layer chromatography for the presence of glycosides, evaporated, and then dried to constant weight. The results of the experiment can be seen from the Table and Fig. 1.

The results of the chromatography of the combined fractions in a thin fixed layer of silica gel are given in Fig. 2.

The results obtained show that Bio-Gel P-2 can be used successfully for the fractionation of the TGF of ginseng in a similar manner to their separation on Sephadex that we have described previously [3].

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CARDENOLIDES OF THE SEEDS OF CORONILLA SCORPIOIDES

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The monoglycoside glucocorotoxigenin has previously been isolated from the seeds of Coronilla scorpioides (L.) Koch., family Leguminosae [1]. In the present paper we give the results of a further investigation of the cardenolides of this plant.

Paper chromatography of extracts of the seeds in the benzene–butanol (2:1)/water system showed the presence of six substances of a cardenolide nature which were arbitrarily designated I (R_f 0.87), II (R_f 0.72), III (R_f 0.64), IV (R_f 0.43), V (R_f 0.20), and VI (R_f 0.08).

To isolate these substances, the comminuted and defatted seeds were extracted with 70% ethanol. The extracts were evaporated to an aqueous residue. The further treatment was carried out by the method described previously [2]. Then the aqueous extract containing the total cardenolides was separated into fractions by means of mixtures of chloroform– ethanol mixtures (9:1, 3:1, and 2:1).

The residues of the evaporation of the 9:1 and 3:1 chloroform-ethanol extracts were separated on a column of alumina. The first extract yielded I and the second yielded II and a small amount of III.

The glycosides of the 2:1 chloroform-ethanol extract were separated by partition chromatography on silica gel (mobile phase water-satured butanol, stationary phase water). III, IV, and V were isolated. In all, five compounds were obtained, three of which were shown to be identical by their physicochemical properties and those of their transformation products, by color reactions with 84% sulfuric acid, IR spectra, and melting points of mixtures.

Substance I was corotoxigenin. $C_{23}H_{32}O_5$, $[\alpha]_D^{20} + 43°$ (c 1.0 ; methanol), mp 220–222° C [3, 4]; II was frugoside, $C_{29}H_{44}O_9$, $[\alpha]_D^{20} - 14.5°$ (c 0.69; ethanol), mp 165–167/234–238° C [4, 5]; and III was frugocorotoxigenin, $C_{29}H_{42}O_{10}$, $[\alpha]_D^{20}$ + 6.5 (c 0.2 ; methanol), mp 273–275° C [1, 6].

Substance IV had a molecular weight of 568 (lactone titration); mp 267–269° C, $[\alpha]_D^{20}$ +8.0° (c 0.1; methanol); acetyl derivative mp 254–258° C, $[\alpha]_D^{20}$ +16.1° (c 0.99; chloroform). Acid hydrolysis by Mannich and Siewert's method [7] cleaved the glycoside into an aglycone of undetermined structure, with mp 141–144° C (from aqueous acetone), $[\alpha]_D^{20}$ +40° (c 0.8; chloroform), and a sugar which, on chromatography in various solvent systems, had R_f values identical with those of D-glucose. This substance is not hydrolyzed by the enzymes of the seeds of C. scorpioides and of the fungus Aspergillus oryzae. The glycoside was reduced with sodium borohydride, which shows the presence of a carbonyl group in its molecule.

Substance V was coronillobioside with a molecular weight of 712 (lactone titration), and neither it nor its acetyl derivative could be crystallized.

The enzymatic hydrolysis [2] of this compound split it into the aglycone corotoxigenin and two molecules of D-glucose.

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17α-HYDROXYSTROPHANTHIDIN

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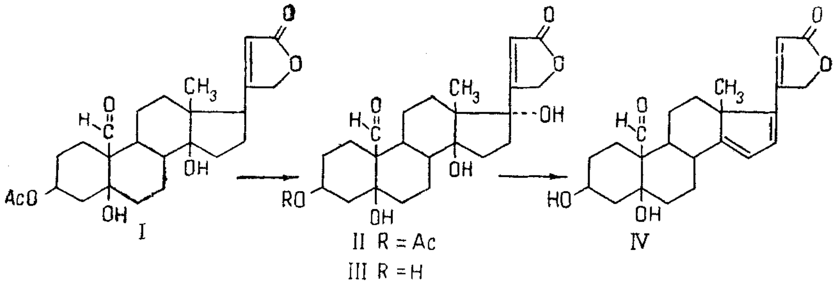
In addition to the obligatory hydroxy groups at C-3 and C-14, many natural cardenolides have additional alcoholic groups in positions 1β, 2α, 5β, 11β, 12α, 12β, 15β, 16β, and 19 of the steroid nucleus [1]. However, in contrast to the vegetable pregnanes and the corticosteroid hormones, cardiac aglycones substituted by a hydroxy group at C-17 are not found in nature.

We have effected the synthesis of 17α-hydroxystrophanthidin (III). For this purpose, strophanthidin acetate (I) was oxidized with selenous acid [2, 3] in boiling dioxane solution for 25 hr; the reaction products yielded II, $C_{25}H_{34}O_8$, with mp 272–275° C (from methanol), $[\alpha]_D^{25}$ −9.9° (c 1.2; pyridine), $[\alpha]_D^{24}$ +17.0° (c 0.1; dioxane); UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 218, 303 mμ (log ε 4.10, 1.61). With Raymond's reagent the substance gives a pink coloration. Compound II is not acetylated under the usual conditions.



I

II R = Ac

III R = H

IV

When the tetraol III was boiled with methanol containing 5% hydrochloric acid for 5 hr, it gave a mixture of substances from which, after separation on a thin-layer chromatogram, product IV was isolated; it was identified chromatographically and also by its UV spectrum [$\lambda_{max}^{C_2H_5OH}$ 338 mμ (log ε 4.20)] as 14, 16-dianhydrostrophadogenin [4].

In biological tests on cats, 17α-hydroxystrophanthidin acetate (II) possessed fairly pronounced activity (LD 1.0 mg/kg), although this was a fifth of the activity of the initial strophanthidin acetate (I) (LD 0.20 mg/kg). All this indicates that the newly introduced hydroxy group occupies the 17α-position.

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