When the glycoside was hydrolyzed with 2% sulfuric acid for 4 hr, an aglycone $C_6H_6O_2$ with mp 170–171° C was obtained. The acetyl derivative $C_{10}H_{10}O_4$ contained two acetyl groups and had mp 121° C.

From its R_f value and its color reactions on paper chromatography in various solvent systems, the aglycone was identical with a reference sample of hydroquinone. Mixtures of the aglycone with hydroquinone and of its acetate with hydroquinone acetate gave no depression of the melting point.

Enzymatic hydrolysis with an enzyme from the fungus Aspergillus oryzae again gave hydroquinone and D-glucose, in equimolecular amounts.

Like arbutin, the glycoside that we had isolated gave a blue coloration with ferric chloride. The R_f values and the nature of the coloration of the glycoside on paper chromatography in various solvent systems coincided with those of a reference sample of arbutin. Mixtures of the glycoside with arbutin isolated from the leaves of Arcostaphylos uva ursi and of their pentaacetates gave no depression of the melting points.

We have also found arbutin in the leaves of S. bracteifolia Stank. and S. xeranthemoides MB.

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SEPARATION OF THE GLYCOSIDES OF GINSENG ON BIO-GEL P-2

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To separate the total glycoside fraction (TGF) from the roots of ginseng (Panax ginseng C. A. Meyer) [1], we have used gel filtration through Bio-Gel P-2 (50–100 mesh) [2].

Distribution of the glycosides in the fractions		Glycosides contained in the fractions (panoxosides)
fraction	g	
1—20	—	—
21—22	0.1158	*D*, *E*, *F* and *G*
23—32	0.1486	*F* and *G*
33—34	0.0078	Traces of *F* and *C*
35—50	0.5076	*A*, *B* and *C*
51—63	0.0723	Traces of *A*, *C* and *F*

The Bio-Gel (200 g), after being swollen in a 0.1 N solution of sodium chloride (24 hr) was transferred to a column (75 × 3.5 cm) and washed with distilled water. One gram of TGF in methanol (5 ml) was transferred to the column and

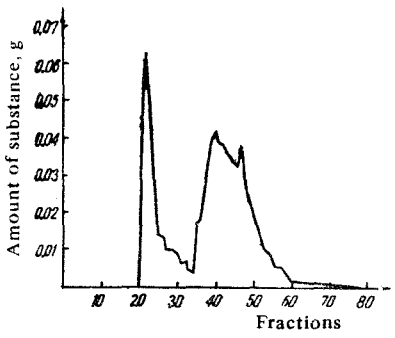

Fig. 1. Distribution of TGF of ginseng on Bio-Gel P-2.

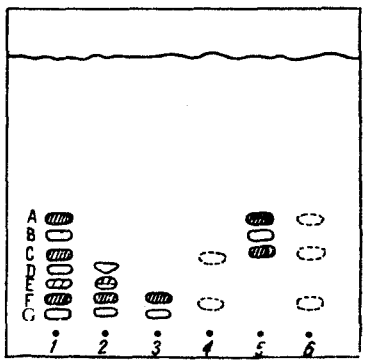

Fig. 2. Thin-layer chromatogram of the combined fraction obtained in the distribution of the TGF of the roots of ginseng on Bio-Gel P-2. 1) TGF; 2) fractions 21-22; 3) fractions 23-32; 4) fractions 33-34; 5) fractions 35-60; 6) fractions 61-63. Solvent system: chloroform–methanol (2:1) saturated with water. Spots visualized with concentrated H_2SO_4.

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, $C_{29}H_{44}O_{10}$, $[\alpha]_D^{20} - 14.5°$ (*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 coroniliobioside 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.