STEROID GLYCOSIDES OF THE ROOTS OF *Capsicum annum*.

III. STRUCTURE OF CAPSICOSIDE E

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We have previously established that the roots of red pepper contain steroid glycosides of the spirostan series [1]. In the present communication we give information on the isolation of two steroid glycosides from pepper roots and the determination of their structures.

As the result of repeated chromatography of a methanolic extract of the roots on a column of silica gel, we isolated two chromatographically individual fractions of glycosides of the spirostan series differing in polarity. After their complete acid hydrolysis, in each case we detected three aglycons: gitogenin, diosgenin, and tigogenin. On the basis of the results obtained, it was assumed that each chromatographically individual fraction consisted of a mixture of gitogenin, diosgenin, and tigogenin glycosides with closely similar structures.

Since attempts at the isolation of individual spirostanol glycosides directly did not give results, we first acetylated each fraction and separated the acetylated glycosides on a silica gel column in the chloroform–acetone (45:5) solvent system.

After the saponification of the peracetates isolated, glycosides were obtained in the individual form which we have called capsicoside D_1 (I), mp 280-282°C, $[\alpha]_D^{20}$ +46° (c 5.3; CH_3OH–$CHCl_3$ (2:1)) and capsicoside E_1 (I), mp 253-254°C, $[\alpha]_D^{20}$ – 67° (c 4.8; CH_3OH–$CHCl_3$ (2:1)). After complete acid hydrolysis (2.5% sulfuric acid, 105°C, 15 H) they gave a single aglycon which was identified by its physicochemical constants as gitogenin. Using PC and GLC [2], in the hydrolysate of (I) galactose, glucose, and xylose were detected in a ratio of 2:1:1, and in the hydrolysate of (II) the same sugars in a ratio of 2:2:1.

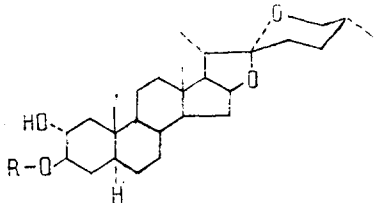
The order of the bonds and the dimensions of the rings of the monosaccharide residues were determined after the Hakomori methylation [3] of (I) and (II) followed by methanolysis of the permethylated derivatives. With the aid of TLC and GLC in the presence of markers, methyl 2,3,4-tri-O-methyl-D-xylopyranoside, methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside, methyl 2,3,6-tri-O-methyl-D-galactopyranoside, and methyl 4,6-di-O-methyl-D-glucopyranoside were detected in the methanolysate of (I), and methyl 2,3,4-tri-O-methyl-D-xylopyranoside, methyl 2,3,6-tri-O-methyl-D-galactopyranoside, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, and methyl 4,6-di-O-methyl-D-glucopyranoside in the methanolysate of (II).

As the aglycon we isolated the 2-monomethyl ether of gitogenin with mp 220-223°C, $[\alpha]_D^{20}$ – 122° (c 0.42; $CHCl_3$); according to the literature: mp 221-224°C, $[\alpha]_D$ – 111° [4], which shows that the carbohydrate chain in these glycosides is attached to C_3 of the aglycon.

The methylation results were confirmed by the periodate oxidation of (I) and (II). After the acid hydrolysis of the oxidized compounds glucose was identified in each case.

To determine the sequence of attachment of the monosaccharide residues, (I) and (II) were subjected to partial hydrolysis (1% sulfuric acid, 100°C, 2 h).

On the basis of the facts presented, and also the results of an investigation of the progenins obtained on partial hydrolysis, the following structures are suggested for capsicosides D_1 and E_1:



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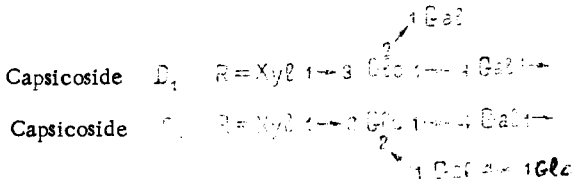

Capsicoside D_1

Capsicoside

The configurations of the glycosidic centers determined from the difference between the molecular rotations of the glycoside and its progenins corresponded to Klyne's rule [5].

Capsicoside D_1 proved to be identical with gitonin [6] isolated previously after the enzymatic hydrolysis of lanotigoside from the leaves of *Digitalis lanata*.

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SYNTHETIC ANALOGUES OF *Peganum* ALKALOIDS.

IV. INTRODUCTION OF BROMINE INTO THE BENZENE RING OF QUINAZOLINES. 6-BROMOPEGANINE AND 6-BROMODEOXYPEGANINE

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The reaction of 4-quinazolones with electrophilic reagents has been studied in fairly great detail [1]: only in the nitration and sulfochlorination reactions does substitution take place in the benzene ring. The substituent then occupies position 6. On the bromination of 2,3-polymethylene-3,4-dihydro-4-quinazolones, no substitution of the benzene ring takes place. Depending on the reaction conditions, perbromides or 9-substituted 4-quinazolines are obtained. Only one reaction has been described for the quinazolone series — nitration [2], in which the nitro group likewise occupies position 6.

We have performed the bromination of the quinazoline alkaloids peganine (Ia) and deoxypeganine (Ib) with bromosuccinimide in glacial acetic acid. The yields of the bromination products (IIa and b) amounted to 50-70%.

Compound (IIa), mp 206°C (decomp.), $[\alpha]_D$ − 97° (c 1.2; chloroform); absorption bands in the UV spectrum of (IIa) (229, 310 nm) showed retention of the quinazoline skeleton, and M^+ 266/268 the fact that a monobromo derivative had been obtained.

Signals in the PMR spectrum ($CDCl_3$, δ, ppm) of product IIa at 4.50 (2H, s), 4.57 (1H, m), 2.15 (2H, m), and 3.20 (2H, m) must be assigned to the protons in positions 4, 9, 10, and 11, respectively. Consequently, the bromine cannot have entered rings B or C. Substitution took place in the benzene ring, A. Judging from the nature of the splitting of the signals of the aromatic protons (6.94, d, J = 3 Hz; 7.17 dd, J = 9.5 Hz, J = 3 Hz; and 6.84, d, J = 9.5 Hz), substitution took place in positions 6 and 7. The choice was made on the basis of the results of a study of a minor product of this reaction.

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