Astragalin (X). Yellow crystals with the composition $C_{21}H_{20}O_{11}$, mp 236-238°C (aqueous ethanol). On acid and enzymatic hydrolysis it was split into glucose and kaempferol (M^+ 286).

This is the first time that compounds (III), (IV), (VI), (VIII), and (IX) have been isolated from common lilac. It is interesting that compounds (V) and (VII) have been isolated previously from the flowers of this plant [3], and compound (X) from lilac leaves, in which, among the flavonoids, rutin predominates [5].

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STEROID GLYCOSIDES OF THE ROOTS OF Capsicum annuum.

IV. STRUCTURE OF CAPSICOSIDES C_2 AND C_3

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Several chromatographically homogeneous fractions containing glycosides – gitogenin, tigogenin, and diosgenin – close in structure and difficult to separate have been isolated previously from the roots of bush red pepper Capsicum annuum L. [1]. Continuing an investigation of the glycosidic fractions of the roots of this plant remaining after the separation of capsicoside C_1, we have isolated another two glycosides, and we give structures for them.

The isolation of individual glycosides of tigogenin and diosgenin by the direct method was unsuccessful, and therefore to separate the mixture of these glycosides the double bond of the diosgenin moiety was epoxidated. The fully acetylated glycosidic fraction obtained was treated with m-chloroperbenzoic acid [2]. The completeness of epoxidation was determined with the aid of TLC and IR spectroscopy. As a result, a new diosgenin glycoside derivative was obtained – an oxirane (I), with mp 135-137°C, $[\alpha]_D^{20}$ −43° (c 1.0; $CHCl_3$), readily separable from the tigogenin glycoside peracetate (II), mp 117-119°C, $[\alpha]_D^{20}$ −68° (c 1.0; $CHCl_3$), by chromatography on a column of silica gel in the solvent system chloroform–acetone–methanol (45:5:2).

The individual peracetate (II) was saponified, and a glycoside was isolated which we have called capsicoside C_2 (III), mp 270-272°C, $[\alpha]_D^{20}$ −40° (c 1.0; CH_3OH). The complete acid hydrolysis of this glycoside gave tigogenin as the aglycon.

The peracetate (I) was then treated with chlorotrimethylsilane and sodium iodide in acetonitrile [3]. The diosgenin glycoside peracetate obtained was purified by chromatography, and saponification led to an individual diosgenin glycoside – capsicoside C_3 (IV), mp 263-265°C, $[\alpha]_D^{20}$ −60° (c 1.0; CH_3OH). Hydrolysis of glycoside (IV) gave one alycon, identical in its physicochemical constants with diosgenin.

To determine the compositions and relative amounts of the monosaccharides in the carbohydrate moieties of the glycosides we studied a hydrolysate of each glycoside with the aid of PC and GLC [4].

In each of the hydrolysates of (III) and (IV), galactose, glucose, and xylose were detected in a ratio of 1:1:1.

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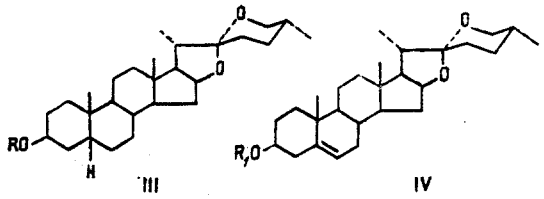
The order of the bonds and the sizes of the rings of the monosaccharides were determined after the Hakomori methylation of (III) and (IV) [5] followed by methanolysis of the permethylated derivatives. By TLC and GLC in the presence of markers, in each of the methanolysates, from (III) and (IV), methyl 2,3,4-tri-O-methyl-D-xylopyranoside, methyl 2,4,6-tri-O-methyl-D-glucopyranoside, and methyl 2,3,6-tri-O-methyl-D-galactopyranoside were identified.

The results of methylation were confirmed by periodate oxidation followed by acid hydrolysis. After these procedures, glucose was detected in the hydrolysates of capsicosides C_2 and C_3.

The sequence of attachment of the carbohydrate fragments in the oligosaccharide chains of these capsicosides was determined on mild acid cleavage with the production of all possible progenins. In the case of the glycoside (III), two progenins were obtained: a monoside (V), mp 289-290°C, $[\alpha]_D^{20}$ −28° (c 0.8; CH_3OH), and a bioside (VI), mp 291-293°C, $[\alpha]_D^{20}$ −37° (c 1.0; CH_3OH). Progenin (V) decomposed into tigogenin and galactose, and progenin (VI) into tigogenin, galactose, and glucose. The partial acid hydrolysis of capsicoside C_3 gave progenin (VII), mp 296-297°C, $[\alpha]_D^{20}$ −63° (c 1.0; CH_3OH), and progenin (VIII), mp 290-291°C, $[\alpha]_D^{20}$ −64° (c 1.3; CH_3OH). The complete decomposition of progenin (VII) gave diosgenin and galactose, and that of progenin (VIII) gave diosgenin, galactose, and glucose. Progenins (V), (VI), (VII), and (VIII) were identical with the known capsicosides A_2, B_2, A_3, and B_3, respectively [6].

The configurations of the glycosidic centers were shown from the difference in the molecular rotations of each capsicoside and its progenins [7].

Thus, for glycosides (III) and (IV) we propose the following structures:



$R = R_1 = \beta\text{-D-Xyl}_p \xrightarrow{3} \beta\text{-D-Glc}_p \xrightarrow{4} \beta\text{-D-Gal}_p$

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