GLYCOSIDES OF *Vaccaria segetalis*

VIII. THE STRUCTURE OF VACSEGOSIDE C

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We have isolated vacsegoside C (I) — a glycoside of gypsogenin (II) with the composition $C_{87}H_{138}O_{49}$, mp 242-245°C (decomp.), $[\alpha]_D^{25}$ + 8.2 ± 3° (c 1.14; water) — from the seeds of *V. segetalis* [1]. The carbohydrate part of (I) consists of D-glucose, D-galactose, D-fucose, L-rhamnose, L-arabinose, D-xylose, and D-glucuronic acid (1 : 2 : 1 : 2 : 1 : 2 : 1, GLC).

The alkaline saponification of (I) (10% KOH) gave a progenin of vacsegoside C (III) with the composition $C_{35}H_{82}O_{24}$, mp 235-240°C (decomp.), $[\alpha]_D^{20}$ −2 ± 2° (c 0.57; water), the acid hydrolysis of which gave D-galactose, D-xylose, and D-glucuronic acid (2 : 1 : 1, GLC), gypsogenin (II), and its β-glucuronoside. D-glucose, L-rhamnose, and D-xylose were found in an acid hydrolyzate of the oligosaccharide (IV) split off. The absence of D-fucose and L-arabinose from the monosaccharides after saponification indicates that one of them may be connected with the carboxy group of the genin and the other with the carboxy group of the uronic acid and undergo degradation on alkaline saponification.

When compound (I) was oxidized with periodate, the D-fucose, D-xylose, and D-glucuronic acid remained unchanged. Consequently, the D-fucose is a center of branching and is connected with the COOH group of the genin. The arabinose is attached to the carboxy group of the glucuronic acid.

The structure of (III) was established on the basis of the results of periodate oxidation, methylation, and partial acid hydrolysis. The progenin (III) was hydrolyzed with 0.3% H_2SO_4. From the hydrolysis products were isolated a trioside of gypsogenin which was identical with the progenin of vacsegoside B in its physical constants, chromatographic behavior, and the results of periodate oxidation and methylation [2]. Thus, for the bond with D-xylose in (III) only the hydroxy group at C_4 of the D-glucuronic acid remains. As a whole, the O-glycosidic chain has the structure shown in the structural formula.

So far as concerns the carbohydrate chain attached to the carboxy group of (II), it contains D-glucose, D-fucose, L-rhamnose (two molecules), and D-xylose. Substances (I) and (IV) were methylated by Hakomori's method. 2,3,4,6-tetra-O-Methyl-D-glucose, 2,3,4-tri-O-methyl-L-rhamnose, 2,4-di-O-methyl-D-xylose, and 2,3-di-O-methyl-L-rhamnose were found in a hydrolyzate of the permethylate of (IV). In a hydrolyzate of the permethylate of (I), in addition to the methylated sugars mentioned above, we found 2,3,4,6-tetra-O-Methyl-D-galactose, 2,3,4-tri-O-methyl-D-xylose, 2,3,4-tri-O-methyl-L-arabinose, 2-O-methyl-D-fucose, and free glucuronic acid. The permethylate of (I) was reduced with lithium tetrahydroaluminate and hydrolyzed. This gave 2-O-methyl-D-fucitol, confirming the linkage of the D-fucose with the carboxy group of (II).

The vacsegoside (I) was hydrolyzed with 5% oxalic acid. This yielded a pentaoside (V) with the composition $C_{59}H_{92}O_{27}$, mp 250-260°C (decomp.) and a heptaoside of gypsogenin (VI) with the composition $C_{70}H_{110}O_{35}$, mp 247-250°C (decomp.), $[\alpha]_D^{20}$ + 20 ± 2° (c 1.2; water). The acid hydrolysis of (V) and (VI) gave gypsogenin, gypsogenin β-D-glucuronoside,

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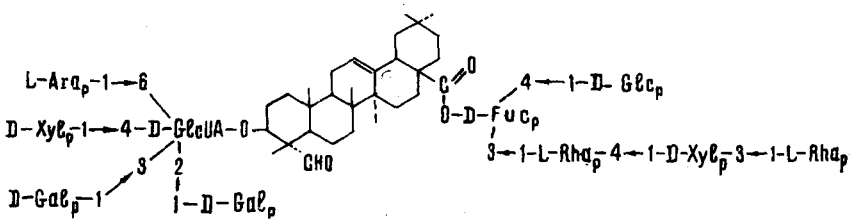
and D-galactose, D-xylose, D-fucose, L-rhamnose, and D-glucuronic acid (two molecules each of xylose and rhamnose). The structure of (V) and (VI) were elucidated on the basis of the results of hydrolytic cleavage, periodate oxidation, and methylation. It was found that the acylosidic moiety of the pentaoside (V) coincided completely with the analogous moiety of vacsegoside B [2], and the acyloside moiety of the heptaoside (VI) differed from the O-acyl chain of the pentaoside (V) by one terminal rhamnose molecule connected with the xylose at C_3—OH. Since the acid hydrolysis of the permethylate of (I) gave 2-O-methyl-D-fucose, only a link with the fourth hydroxyl of D-fucose remains for the glucose in (I).



On the basis of the facts presented, the above structure may be put forward for vacsegoside C.

LITERATURE CITED

1. R. T. Baeva, M. O. Karryev, K. Amanmuradov, and N. K. Abubakirov, Khim. Prirodn. Soedin., 258 (1974).
2. R. T. Baeva, M. O. Karryev, and N. K. Abubakirov, Khim. Prirodn. Soedin., 804 (1974).