GLYCOSIDES OF Vaccaria segetalis

VII. STRUCTURE OF VACSEGOSIDE B

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We have previously reported the isolation from the seeds of Vaccaria segetalis of triterpene glycosides—vacsegosides A, B, C, and D [1]. The present paper gives results going to prove the structure of vacsegoside B.

Vacsegoside B (I), $C_{70}H_{110}O_{36}$ is a crystalline, readily water-soluble substance with mp 250-251°C (decomp.), $[\alpha]^{25}_{D}$ +23.9 ± 3° (c 0.92; water). The hydrolytic cleavage of the glycoside (I) with 18% hydrochloric acid gave gypsogenin with mp 271-273°C, $[\alpha]^{20}_{D}$ +92.0° (c 1.5; ethanol). On hydrolysis with 2% sulfuric acid, gypsogenin β-D-glucuronoside – vaccaroside [2] – with mp 203-205°C (decomp.), $[\beta]^{20}_{D}$ + 17.2 ± 2° (c 1.03; ethanol), was isolated.

The carbohydrate moiety of vacsegoside B was found by the gas–liquid chromatography (GLC) of the trimethylsilyl ethers of the methyl glycosides to contain D-galactose, L-rhamnose, D-fucose, D-xylose, L-arabinose, and D-glucuronic acid (2 : 1 : 1 : 1 : 1 : 1).

When the glycoside (I) was saponified with 10% alkali, we obtained an oligosaccharide (III) and a gypsogenin trioside (II), $C_{48}H_{74}O_{20}$, with mp 245-250°C (decomp.), $[\alpha]^{25}_{D}$ + 26.0 ± 2° (c 1.0; water), the acid hydrolysis of which gave D-galactose and D-glucuronic acid (2 : 1; GLC). On acid hydrolysis of the oligosaccharide (III), L-rhamnose and D-xylose were identified. The absence of D-fucose and L-arabinose from among the monosaccharides after alkaline saponification shows that the first of them is bound to the carboxy group of the genin and the second to the carboxy group of the uronic acid, and that they undergo degradation under the action of alkali.

Glycosides (I) and (II) were oxidized with sodium periodate. The oxidation products were hydrolyzed. The hydrolyzate of the oxidation products of the glycoside (I) were found by PC and TLC to contain fucose and glucuronic acid, and the hydrolyzate of (II) to contain glucuronic acid. Consequently, the fucose and glucuronic acid are centers of branching or are substituted at the hydroxyls in positions 3.

Compounds (I-III) were methylated by Hakomori's method. This gave the permethylates (IV-VI), which were hydrolyzed in 5% methanolic sulfuric acid. In the hydrolyzate of the permethylate (IV) by PC in the water-saturated methyl ethyl ketone system and by TLC in the benzene–acetone (2 : 1) system we identified 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, 2,3-di-O-methyl-L-rhamnose, 2,4-di-O-methyl-D-fucose, and 4-O-methyl-D-glucuronic acid. When (IV) was subjected to reductive cleavage with lithium tetrahydroaluminate, the latter two sugars were reduced to 2,4-di-O-methyl-D-fucitol and to 4-O-methyl-D-glucose. In the hydrolyzate of the permethylate (V) we found 2,3,4,6-tetra-O-methyl-D-galactose (two moles) and methyl 4-O-methyl-D-glucuronate, and in the hydrolyzate of (VI) 2,3,4-tri-O-methyl-D-xylose and 2,3-di-O-methyl-L-rhamnose.

The results of methylation were confirmed by the results of periodate oxidation, in which the glycoside absorbed nine moles of periodate and liberated about four moles of formic acid. Thus, the formula of vacsegoside B can be represented in the following way:

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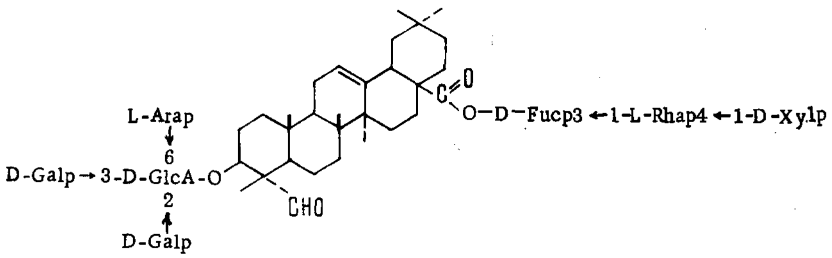

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1. R. T. Baeva, M. O. Karryev, K. Amanmuradov, and N. K. Abubakirov, Khim. Prirodn. Soedin., 258 (1974).*
2. N. K. Abubakirov and K. Amanmuradov, Zh. Obshch. Khim., 34, 1661 (1964).

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*In the Consultants Bureau translation of this article, vacsegoside was erroneously called vaccegoside — Publisher.