GLYCOSIDES OF Vaccaria Segetalis. VI.

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From a methanolic extract of the seeds of Vaccaria Segetalis (Neck.) Carcke, family Caryophyllaceae, we have isolated two triterpene glycosides and have called them segetoside and vaccegoside [1, 2]. A partial structure has been given for the latter [3].

In a further study of the structure of vaccegoside, it was found that this substance is not an individual compound but consists of a mixture of chromatographically very close substances. Only repeated chromatography on columns of silica gel (KSK) in the chloroform–ethanol–water (65 : 35 : 8) system permitted the isolation from this mixture in the individual form of four glycosides which we have called in order of increasing polarity vaccegosides A, B, C, and D.

The acid hydrolysis of all the glycosides with 18% hydrochloric acid gave gypsogenin as the aglycone. In chloroform– methanol (25 : 1 and 10 : 1) systems in a thin layer of silica gel (TLC), the genin gave a mixture of several substances, which is apparently due to the interconversions of gypsogenin, gypsogenin lactone, and 13-α-hydroxy-12,13-dihydrogypsogenin, as has been reported previously [4]. In the hydrolyzates we found, for vaccegosides A and B, D-glucuronic acid, D-galactose, L-arabinose, D-xylose, D-fucose, and L-rhamnose; for vaccegoside C, D-glucuronic acid, D-galactose, L-arabinose, D-xylose, D-fucose, L-rhamnose, and D-glucose; and for vaccegoside D, D-glucuronic acid D-galactose, D-glucose, D-xylose, D-fucose, and L-rhamnose which were identified by direct comparison with authentic samples by paper chromatography and TLC in various solvent systems.

When they were hydrolyzed with dilute acid (2% H_2SO_4, 100°C, 3 h), all the vaccegosides gave the same progenin–gypsogenin 3-β-D-glucuronoside (vaccaroside) [1]–from which it follows that in all the glycosides the glucuronic acid residue is attached directly to the hydroxy group of the genin by a glycosidic bond.

We did not observe for the vaccegosides the mutual transitions of the aldehyde form into the semiacylal form and conversely, as has been reported in the literature [4-6], which is probably due to the absence of a free carboxy group in the glucuronic acid and its possible glycosidation at this carboxy group.

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