A GLYCOSIDE OF GOSSYPOL

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Gossyfiolin – the first of the water soluble satellites of gossypol, which hydrolyzes to gossypurpurin and sugars – has been isolated previously [1] from the glandules of stored cotton seeds [1]. Since in this case the capacity of the gossyfiolin for dissolving in water may be due to the presence of sugars, we decided to obtain a derivative of gossypol itself with a sugar.

The preparation of a gossypol glycoside is complicated by the fact that the gossypol molecule contains six reactive hydroxy groups, while only one sugar residue is generally added to the aglycone molecule in the synthesis of glycosides.

The synthesis of the glycoside was effected by the reaction of tetra-O-acetyl-α-D-galactosyl bromide [2-4] with gossypol by the Koenigs–Knorre method in Chernobai's modification [5]. The product consisted of a light yellow resinous substance which darkened in the air.

The IR spectrum of the substance (Fig. 1, curve a) showed very strong absorption of the carbonyls of the acetyl groups and the presence of hydroxy groups. This permits the assumption that in the gossypol the phenolic hydroxy groups have been substituted incompletely. The results of a chromatographic and IR-spectrophotometric study of the products of deacetylation of the compound obtained performed by various methods (with a solution of ammonia in methanol, with sodium methoxide, with barium methoxide, and with potassium bicarbonate) showed that, in the first place, the acetyl groups were not always removed similarly and completely (Fig. 1, curve b) and, in the second place, that hydrolysis with the splitting of the sugar took place simultaneously with deacetylation.

Examples of similar behavior of phenol glycosides in an alkali medium have been described in the literature [6, 7]. Thus, under the action of catalytic amounts of barium methoxide the tetra-O-acetyl-D-glucoside of 4-hydroxycoumarin is converted into the aglycone and methyl D-glucoside.

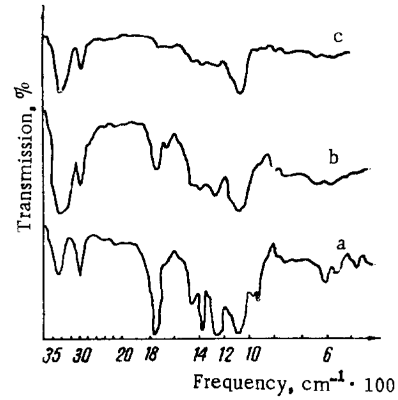

Fig. 1. IR spectra of acetylated gossypol galactoside (a), the partially deacetylated galactoside (b), and gossypol galactoside (c).

We have succeeded in selecting conditions (action of a 2.2% aqueous solution of potassium bicarbonate for 12 days with subsequent freeze-drying) under which, in addition to hydrolysis products (galactose, gossypol, and the products of its transformation), a gossypol galactoside was obtained in the form of a light brown resinous substance readily soluble in ethanol and in an aqueous solution of ethanol but insoluble in water (Fig. 1c). The nature of this substance was shown by IR spectroscopy, thin-layer and paper chromatography, and hydrolysis.

On the basis of the properties of the comparatively well-studied [8] methyl ethers of gossypol, it may be assumed that the formation of tetra- and hexasubstituted derivatives is possible in them. However, the properties of the substance obtained, the stereochemistry of gossypol, and the steric hindrance arising with the introduction of acetylated sugar residues make the substitution of

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all six hydroxy groups impossible, in our opinion. All that has been said above permits the product obtained to be regarded as a gossypol tetragalactoside.

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