STEROID GLYCOSIDES.

THE STRUCTURE OF MELONGOSIDE K FROM THE SEEDS OF *Solanum melongena*

S. A. Shvets and P. K. Kintya

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There is information in the literature on the presence in the seeds of *Solanum melongena* L. (eggplant) of steroid aglycones — diosgenin and tigogenin [1, 2]. In the present communication we give information on the isolation and proof of the structure of a new glycoside — melongoside K (I) — isolated from the seeds of this plant.

As the result of the repeated chromatographic separation of a methanolic extract on a column of silica gel, a chromatographically individual fraction of glycosides was isolated which gave a positive reaction with the Sannie reagent [3] and a negative reaction with the Ehrlich reagent [4], indicating their spirostanol nature. After acid hydrolysis, two aglycones were detected. The aglycones isolated were separated in a thin layer of silica gel impregnated with 2% of $AgNO_3$ in the CH_2Cl_2—$(CH_3)_2CO$ (49:1) system and were identified as tigogenin, mp 202-203°C, $[\alpha]_D^{20}$ −65° (c 1.0; $CHCl_3$), M^+ 416, and diosgenin, mp 208°C, $[\alpha]_D^{20}$ −120° (c 1.0; $CHCl_3$), M^+ 414. On the basis of the results obtained, it was suggested that the fraction consisted of a mixture of glycosides of diosgenin and of tigogenin. To isolate individual compounds, the mixture of lycosides was acetylated, and the diosgenin glycoside was epoxidated at the double bond by the method of Grant and Weavers [5]. After chromatographic separation of the reaction mixture on a column of silica gel in the $CHCl_3$—$(CH_3)_2CO$ (45:5) system, a diosgenin epoxide glycoside peracetate (II) was obtained with mp 146°C, $[\alpha]_D^{20}$ −123° (c 1.0; $CHCl_3$). Compound (II) was de-epoxidated [6], the product was purified chromatographically, and the peracetate of melongoside K (III) was isolated, with mp 135°C, $[\alpha]_D^{20}$ −57° (c 1.0: $CHCl_3$). After the saponification of (III) with 10% NaOH in methanol (90°C, 4 h), the individual glycoside melongoside K was obtained with mp 293°C, $[\alpha]_D^{20}$ −96° (c 1.0; CH_3OH).

After the hydrolysis of (I) with 2.5 Na_2SO_4, the hydrolysate was shown by PC and by the GLC of the acetates of the aldononitrile derivatives of the sugars to contain glucose, galactose, and rhamnose in a ratio of 2:1:1. Diosgenin was identified as the aglycone. Consequently, melongoside K is a diosgenin tetraoside.

When (I) was subjected to Hakomori methylation [7] followed by methanolysis of the peracetates, methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside, methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside, methyl 2,3,6-tri-O-methyl-D-glucopyranoside, and methyl 4,6-di-O-methyl-D-glucopyranoside were identified by TLC and GLC in the presence of markers. The presence of the dimethylglucose showed branching of the carbohydrate chain.

To determine the sequence of attachment of the monosaccharide residues, compound (I) was subjected to partial hydrolysis with 1% H_2SO_4 in methanol (1.5 h). The hydrolysis products were chromatographed on a column of silica gel in the $CHCl_3$—CH_3OH (4:1) system, and three progenins — (IV), (V), and (VI) — were obtained. The hydrolytic cleavage of (IV) and (V) gave diosgenin and glucose, and that of (VI) gave diosgenin, glucose, and galactose in a ratio of 1:2:1. The permethylate obtained as the result of the methylation of (IV) and methanolysis was identified as methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, the permethylates from (V) as methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside and methyl 3,4,6-tri-O-methyl-D-glucopyranoside, and those from (VI) as methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside, methyl 2,3,6-tri-O-methyl-D-glucopyranoside, and methyl 3,4,6-tri-O-methyl-D-glucopyranoside.

On periodate oxidation of the glycoside under investigation followed by acid hydrolysis of the oxidized product, the glucose remained unchanged, which confirmed the results of methylation.

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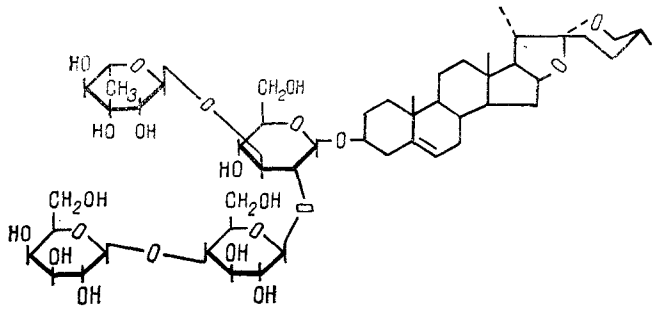
The configurations of the glycosidic centers determined from molecular rotation differences of the glycoside and its progenins corresponded to Klyne's rule [8].

On the basis of the facts presented, the following structure is proposed for melongoside K:



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