STEROID SAPONINS AND SAPOGENINS OF Allium

IX. THE STRUCTURE OF AGINOSIDE

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Continuing a study of the more polar fractions of a methanolic extract of the skins of the bulbs of Allium giganteum Regel. (family Alliaceae) [1, 2] we have isolated a new steroid glycoside which we have called aginoside (I). According to its IR spectrum, glycoside (I) belongs to the spirostan compounds of the 25R series.

When the glycoside was hydrolyzed with weak hydrochloric acid, agigenin (III) [2] was identified as the aglycone. By GLC [3, 4], D-xylene, D-glucose, and D-galactose in a ratio of 1:2:1 were found in the hydrolyzate.

In a study of the products of the Smith degradation of the glycoside (I) [5], we identified D-glucose and agigenin (III). Consequently, one of the two molecules of the glucose either is a center of branching of the carbohydrate chains or has a 1+3 bond.

After acid hydrolysis, the permethylate (II) of the glycoside (I), obtained by Hakomori's method [6], gave dimethoxyagigenin (IV) and a mixture of various methylated monosaccharides. The mixture was separated by chromatography on silica gel. On the basis of the combination of the physicochemical constants, some chemical reactions, and GLC and TLC, the methylated carbohydrates were identified as 2,3,4-tri-O-methyl-D-xylopyranose, 2,3,4,6-tetra-O-methyl-D-glucopyranose, 2,3,6-tri-O-methyl-D-galactopyranose, and 4,6-di-O-methyl-D-glucopyranose. These facts and the results of the Smith degradation of the glycoside (I) permit the conclusion that the center of branching is glucose, and galactose is attached directly to the aglycone.


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Further information on the structure of the carbohydrate chain of aginoside (I) was obtained by studying the products of its partial acid hydrolysis. From these it was possible to isolate three glycosides (VI—VIII). According to GLC, glycoside (VI) is a monoside and contains only galactose. Compound (VII) is a bioside containing galactose and glucose (1:1). Substance (VIII) is a triside, the carbohydrate chain of which consists of one molecule of galactose and two molecules of glucose.

To determine the position of attachment of the terminal sugars glucose and xylose in (I), the triside (VIII) was also subjected to exhaustive methylation by Hakomori's method. In the products of the hydrolysis of the permethylate (IX), 2,3,4,6-tetra-O-methyl-D-glucopyranose, 3,4,6-tri-O-methyl-D-glucopyranose, and 2,3,6-tri-O-methyl-D-galactopyranose were identified. Consequently, in the carbohydrate chain of aginoside (I) the terminal glucose and xylose molecules substitute the hydroxyls at C2 and C3, respectively, of the second glucose molecule, which, in its turn, is attached to the hydroxyl at C6 of galactose.

The configuration of the glycosidic centers is given on the basis of a study of the NMR spectrum (Fig. 1) of the permethylate (II), in which four doublets (a, b, c, and d) of the anomeric protons of the sugars clearly appear in the 4.3—5.2 ppm region. The coupling constants (J = 7—8 Hz) of the signals given show the β configurations of all four glycosidic bonds [7, 8]. The proposed configurations agree with those calculated by the method of molecular rotation differences [9].

A similar carbohydrate chain, called lycotetraose [10] has previously been found in the steroid glycoalkaloids tomatine and dimessine [10], and also in the steroid saponins F-gitonin [11] and purpureagitoside [12].

It was necessary to determine the position of attachment of the carbohydrate chains to the steroid nucleus. Although the most probable position was the hydroxyl at C3, it was not excluded that the sugar moiety was attached to one of the hydroxyls at C2 and C6 of the steroid nucleus. For an unambiguous answer to the question, the dimethoxyagigenin (IV) obtained by the hydrolysis of the permethylate (II) was oxidized with chromium trioxide. The optical rotatory dispersion (ORD) curve of the dimethoxy ketone (V), with a positive Cotton effect (see Experimental), has the form characteristic for 2-oxo- or 3-oxo-5α-steroids [13]. In view of the fact that in the determination of the ORD in methanol with the addition of hydrochloric acid a sharp decrease in amplitude is observed, compound (V) can be considered to be a 3-oxo-5α-steroid [14]. Thus, the carbohydrate residue is attached to the hydroxyl at C3. Consequently, aginoside has the structure corresponding to formula (I).

**EXPERIMENTAL**

Thin-layer chromatography (TLC) was performed on a fixed layer of KSK silica gel containing 7% of gypsum. The following solvent systems were used: 1) butanol—ethanol—water...