TRITERPENE GLYCOSIDES OF *Scabiosa soongorica*

III. THE STRUCTURE OF SONGOROSIDES M AND O

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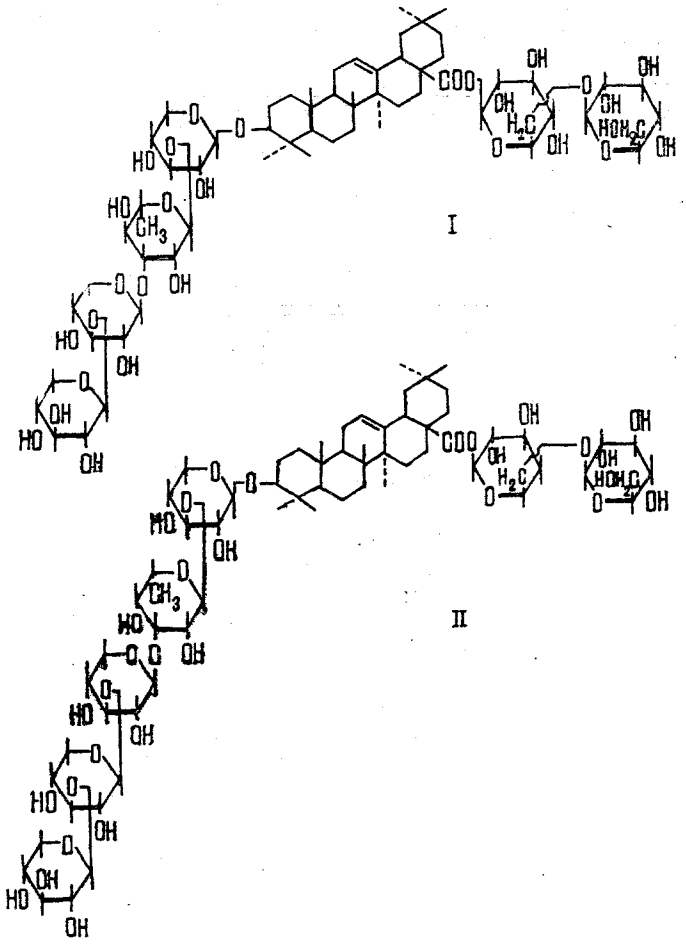
We have previously [1] reported the determination of the structure of songorosides C, G, and I from the roots of *Scabiosa soongorica*. In the present paper we give information on the structure of songorosides M and O.

From the results of acid hydrolysis and gas–liquid chromatography of the silyl derivatives of the methyl glycosides, the sugar moieties of both glycosides consist of L-rhamnose, D-glucose, and D-xylose in a ratio of 1:2:3 for songoroside M and 1:2:4 for songoroside O. Consequently, songoroside M, $C_{63}H_{102}O_{29}$, is a hexaoside and songoroside O, $C_{68}H_{110}O_{33}$, is a heptoaside of oleanolic acid. When these songorosides were subjected to periodic oxidation, L-rhamnose and D-xylose remained unchanged.



I

II

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In the hydrolyzates of completely methylated songorosides M and O we found the same set of methylated sugars: 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,4-tri-O-methyl-D-glucose, 2,3,4-tri-O-methyl-D-xylose, 2,4-di-O-methyl-D-xylose, and 2,4-di-O-methyl-L-rhamnose.

Alkaline saponification of the glycosides showed that songorosides M and O are acylosides. The corresponding progenins were isolated from the products of their alkaline hydrolysis.

On the basis of the results of acid hydrolysis and gas–liquid chromatography, and also exhaustive methylation followed by hydrolysis of the permethylates, it was established that the progenin of songoroside M is identical with songoroside G and the progenin of songoroside O with songoroside I (I).

In alkaline hydrolyzates of both glycosides we found D-glucose. When the glycosides were hydrolyzed with 0.5% sulfuric acid, in the products of hydrolytic cleavage, among other sugars, we found gentiobiose, which is present in the acyloside moiety of the molecule. For songoroside M we propose structure (I), and for songoroside O (II).

For the large set of scabious glycosides, the structures of five of which have been established definitively and those of two provisionally, it is not difficult to trace the obvious biochemical link between them. All the compounds are glycosides of the same aglycone — oleanolic acid. The richest in sugars are songorosides M and O, which form the bulk of the total glycosides and are easy to detect. To songorosides M and O correspond their progenins — songorosides G and I. They are found in the plant in considerable amounts in the native form. By separating the intermediate compounds it is easy to trace by what route of successive growth the elongation of the O-glycosidic chain of carbohydrates takes place from the monoside (oleanolic acid D-xylopyranoside) to the pentoaside (songoroside I). Only in the bioside songoroside C is the terminal monosaccharide L-rhamnose, and then the chain of carbohydrates increases through the addition of D-xylose. The passage to the acylosides, i.e., songorosides M and O takes place by the addition of a complete block — gentiobiose — directly to the carboxy group of the genin. On this occasion, the block is small, consisting only of two molecules of D-glucose. Basically, the biogenetic pattern of the interaction of the triterpene glycosides of *S. soongorica* is similar to that of the glycosides of *Leontice eversmannii* [2], *Ladyginia bucharica* [3], and *Gleditschia triacanthos* [4].

EXPERIMENTAL

For the conditions of chromatography, see [1].

Acid Hydrolysis of Songorosides M and O. Songoroside M (50 mg) was hydrolyzed in 10 ml of a 7.5% aqueous methanol (1:1) solution of sulfuric acid at 90°C for 6 h. The precipitate, after recrystallization from ethanol, had mp 301-305°C, $[\alpha]_D^{20}$ + 78.5 ± 2° (c 1.58; absolute ethanol) and according to TLC in system 6 was identical with oleanolic acid. In the hydrolyzate after neutralization with barium carbonate, L-rhamnose, D-glycose, and D-xylose were found by PC in system 4 and TLC in system 5.

The acid hydrolysis of songoroside O by the method described above gave a similar result.

Songorosides M and O (10 mg each) were heated separately with 5 ml of 0.5% aqueous methanolic sulfuric acid at 90°C for 30 min. After neutralization, gentiobiose was found in the hydrolyzates of both glycosides by TLC in systems 4 and 5.

Periodate Oxidation of Songorosides M and O. Each glycoside (30 mg) was oxidized with a 1% solution of sodium metaperiodate at 6°C for 49 h. The excess of periodate was destroyed with ethylene glycol, the solution was evaporated to dryness, and the residue was extracted with methanol. The methanolic extracts were hydrolyzed with 7.5% sulfuric acid. After neutralization with AV-17 anion-exchange resin (OH^- form), L-rhamnose and D-xylose were found in the hydrolyzates of both glycosides by TLC in system 5.

Methylation of Songorosides M and O. Songoroside M (200 mg) was methylated by Hakomori's method. The permethylate was heated in a 7.5% aqueous methanolic (1:1) solution of H_2SO_4 (100°C, 6 h). The mixture was diluted with water, the methanol was distilled off, and the solution was heated for another 2 h. In the hydrolyzate after neutralization, 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,4-tri-O-methyl-D-glucose, 2,3,4-tri-O-methyl-D-xylose, 2,4-di-O-methyl-L-rhamnose, and 2,4-di-O-methyl-D-xylose were identified by TLC in systems 7 and 8 with markers. Songoroside O was methylated similarly, and the same set of methylated

sugars was found in the products of the hydrolysis of the permethylate in the presence of markers.

Alkaline Hydrolysis of Songorosides M and O. A mixture of 100 mg of songoroside M and 10 ml of 10% aqueous ethanolic (1:1) caustic potash was heated in the boiling water bath for 8 h. For neutralization, the mixture was passed through a column of carboxymethylcellulose (H form). The progenin produced was eluted with system 2. The eluate was evaporated, and an oleanolic acid tetraoside was obtained with mp 249-253°C, $[\alpha]_D^{20} - 27.5 \pm 2°$ (c 0.8; methanol). On chromatography in systems 1, 2, and 3 and by a mixed melting point, the tetraoside was identified as songoroside G. By the method described above, songoroside O yielded an oleanolic acid pentaoside with mp 228-231°C, $[\alpha]_D^{20} - 22.4 \pm 2°$ (c 1.29; methanol). From its chromatographic behavior and a mixed-melting point, the pentaoside was identical with songoroside I.

After the progenins had been obtained, the residual sugars were eluted from the column with aqueous methanol (1:1). D-Glucose was found in the dried eluate by TLC in system 5.

Determination of the Structures of the Products of the Alkaline Hydrolysis of Songorosides M and O. Separately, the tetraoside and pentaoside from the preceding experiment (10 mg each) were hydrolyzed in a 7.5% solution of sulfuric acid at 90°C for 5 h. L-Rhamnose and D-xylose were found in the hydrolyzates of both glycosides after neutralization.

The tetraoisde and pentaoside (20 mg each) were methylated by Hakomori's method. 2,3,4-Tri-O-methyl-D-xylose, 2,4-di-O-methyl-D-xylose, and 2,4-di-O-methyl-L-rhamnose were identified in the hydrolysis products of the permethylates of each of these compounds, investigated separately, by TLC in systems 7 and 8 with markers.

SUMMARY

The structures of songorosides M and O — a hexaoside and heptaoside of oleanolic acid, respectively — have been established. Both glycosides contain gentiobiose in the acyloside moiety. The glycosidic carbohydrate chains of songorosides M and G attached to the C_3 hydroxyl are identical. The O-glycosidic sugar components of songorosides O and I are also identical.

LITERATURE CITED

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