STEROID GLYCOSIDES.

XVI. THE STRUCTURES OF ASPARAGOSIDES C AND E FROM *Asparagus officinalis*

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We have previously [1] reported the isolation of steroid glycosides from *Asparagus officinalis* L. (garden asparagus) and the proof of the structures of asparagosides A and B.

In the present paper we give information on the structures of asparagosides C (I) with mp 287-290°C, $[\alpha]_D^{20}$ −13° (c 0.43; MeOH and E (II) with mp 254-260°C, $[\alpha]_D^{20}$ −38° (c 1.05; H_2O).

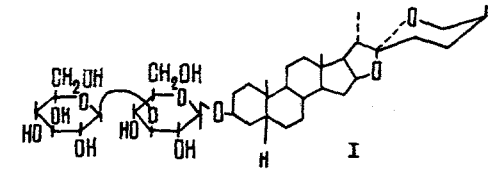
Only asparagoside E gave a positive reaction with Ehrlich's reagent.

The acid hydrolysis of (I) and (II) formed an aglycone which was identified as sarsasapogenin by its specific rotation, $[\alpha]_D^{20}$ −74° (c 0.95; $CHCl_3$), mp of 199-200°C, mass spectrum (M^+ 416), IR spectrum (912 > 892 cm^{-1} with an intensity ratio of 3:1), and chromatographic mobility. In both cases, only glucose was found in the hydrolyzate by paper and gas–liquid chromatography.

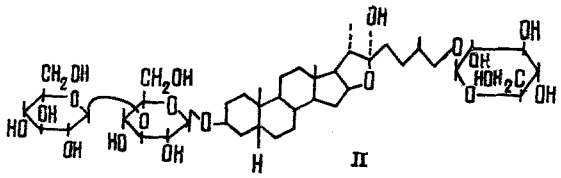
When (I) and (II) were methylated by Hakomori's method [3], followed by methanolysis of the products obtained, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside and methyl 2,4,6-tri-O-methyl-D-glucopyranoside were isolated, being identified by TLC and GLC in the presence of markers. On periodate oxidation followed by hydrolysis, in the case both of asparagoside C and of asparagoside E the glucose was unaffected, which confirms the results of methylation. The partial hydrolysis of (I) gave a monoside identical with asparagoside A [1] and sarsasapogenin, and the partial hydrolysis of asparagoside E gave asparagoside C, in addition.

The enzymatic hydrolysis of (II) with the β-glucosidase from *Helix pomatia* (12 h at room temperature) gave asparagoside C. Peracetylated (II) was subjected to oxidative cleavage by the method of Tschesche et al. [4] and yielded methyl δ-hydroxy-γ-methylvalerate tetraacetylglucoside. This shows that asparagoside E has a furostanol structure and is the prototype (I).

On TLC in methanolic systems (II) behaved in the same way as glycosides of the furostanol series [4].



I



II

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The configuration of the glycosidic centers determined from molecular rotation differences of the glycosides themselves and their progenins correspond to Klyne's rule [5]. On the basis of the facts presented, the preceding structures are proposed for asparagosides C and E.

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STEROID SAPONINS FROM THE ROOTS OF *Asparagus verticillatus*

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A preliminary phytochemical investigation showed that the roots of *Asparagus verticillatus* L. (family Liliaceae) collected on the Apsheron peninsula in the fruit-bearing period contained a considerable amount of steroid saponins [1, 2].

After the raw material had been defatted with chloroform and petroleum ether, the saponins were extracted with 80% methanol.

To study the qualitative composition of the steroid saponins, the methanolic extract was concentrated and was subjected to chromatography in a thin layer of silica gel in the water-saturated butanol and chloroform–methanol–water (65:35:10) systems. This showed the presence of five individual saponins — A, B, C, D, and E.

In order to study the nature of the sapogenin, the purified total saponins were subjected to hydrolysis with 10% H_2SO_4 at 90°C for 8 h. After filtration and washing with water, the sapogenin was dissolved in methanol and the presence of one genin in it was established chromatographically.

As the result of repeated recrystallization from ethyl acetate, colorless transparent acicular crystals of the genin were obtained with mp 198-200°C, $[\alpha]_D^{20}$ −76° (c 0.8; methanol). A consideration of its spectral characteristics in the IR region showed that the spiroketal group of the genin isolated belonged to the nor series [3], and the genin itself proved to be chromatographically identical with sarsasapogenin, which is in harmony with literature information [4, 5].

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