STRUCTURE OF THE GLYCOSIDES OF *Asparagus officinalis* THE STRUCTURE OF ASPARAGOSIDES A AND B

G. M. Goryanu, V. V. Krokhmalyuk, and P. K. Kintya

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From a methanolic extract of the roots of Asparagus officinalis L. (garden asparagus) after purification on silica gel and Sephadex we isolated the combined steroid components, consisting of eleven compounds. On studying the free steroids by means of TLC and GLC, it was found that two compounds are β-sitosterol and sarsasapogenin. The remaining nine compounds proved to be steroid glycosides and we have called them in order of increasing polarity asparagosides A, B, C, D, E, F, G, H, and I. All the glycosides gave a positive reaction with the Sannié reagent [1]. Only asparagosides B, E, G, H, and I gave a positive reaction with the Ehrlich reagent [2]. Consequently, according to preliminary results, they can be assigned to glycosides of the furostanol series, and asparagosides A, C, D, and F to the spirostanol series. On a fixed layer of silica gel in methanol-containing systems, asparagoside B, E, G, H, and I each give two spots, which is in harmony with information in the literature [3] for furostanol glycosides, and in butanol-containing systems they each give one spot.

Although after acid hydrolysis sarsasapogenin was identified as the aglycone for all the asparagosides by comparison with markers using TLC and GLC [4], the native genin for asparagosides B, E, G, H, and I is actually (25S)-5β-furostan-3β,22α,26-triol.

As the monosaccharide component, by paper and gas chromatography we identified only glucose for asparagosides A, B, C, D, G, and E, and glucose and xylose for the glycosides F, H, and I. Saponin A has mp 243-245°C, $[\alpha]_D^{20} - 62°$ (c 0.8; methanol), and saponin B mp 152-155°C, $[\alpha]_D^{20} - 81°$ (c 1.0; methanol).

As a result of the methanolysis of the permethylated glucosides A and B by Hakomori's method [5], in the presence of authentic markers by the GLC method in both cases we identified only methyl 2,3,4,6-hexa-O-methyl-D-glucoside. The molecular weight obtained of 574 (calculated 596) in relation to the yield of genin shows that asparagoside B contains only one glucose molecule. The fact that glucoside B belongs to the furostanol series is also confirmed by its reduction with $NaBH_4$ followed by acid hydrolysis, with the production of dihydrosarsasapogenin [3]. Under such conditions, spirostanols are not hydrogenated [6]. The configuration of the glycosidic centers was given by means of Klyne's rules [7].

On the basis of the results obtained, it may be considered that asparagoside A is 3-O-β-D-glucopyranosyl-(25S)-5β-spirostan-3β-ol and is identical with the sarsasapogenin monoside obtained previously by the partial hydrolysis of parillin [8], and asparagoside B is 26-O-β-D-glucopyranosyl-(25S)-5β-furostan-3β,22α,26-triol.

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SAPOGENINS OF Eryngium macrocalyx

M. T. Ikramov, I. A. Kharlamov,
R. L. Khazanovich, and Kh. Kh. Khalmatov

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Continuing a study of plants of the genus Eryngium L. (eryngo), we have isolated the total saponins from the roots of E. macrocalyx Schrenk. We used the procedure employed for isolating the saponins from the roots of E. octophyllum Eug. Kor. [1].

Acid hydrolysis of the saponins isolated gave the combined sapogenins. The sapogenins were separated on a column of silica gel, from which they were eluted with a mixture of chloroform and ethyl acetate with a gradient of increasing concentrations of ethanol (from 1 to 10%). Two substances were obtained in the individual state. The first substance (mol. wt. 572), from its R_f values [0.58 in chloroform–ethyl acetate (2 : 1); 0.50 in benzene–chloroform–methanol (3 : 3 : 0.5); 0.67 in chloroform–methanol (11 : 1)] and melting point (220–223°C), the melting point of its acetate (113–116°C), its IR spectrum, and a mixed melting point, was identical with eryngiumgenin A, which we have isolated previously from E. octophyllum [2].

The second substance was identified on the basis of its R_f values, melting point, melting point of its acetate, and mass and IR spectra as oleanolid acid.

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