

# A CHEMICAL STUDY OF THE STEROID GLYCOSIDES

OF *Tribulus terrestris*

## IV. STEROID SAPONINS

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We have continued a study of the steroid glycosides of *Tribulus terrestris* L. (puncture vine), family Zygophyllaceae. On the basis of their physicochemical constants and also a comparison of their chromatographic mobilities with markers kindly given to us by Prof. Kawasaki, saponins A, B, C', and C isolated from this plant previously [1] have been identified as, respectively, trillin [2], diosgenin D-glucosido-D-glucoside [3], gracillin [4], and dioscin [5].

Chromatographic purification of the water-soluble glycoside led to the production of two substances in the pure state: a main saponin D and a minor saponin E. These glycosides gave a positive reaction with Ehrlich's reagent, which shows that they belong to compounds of the furastanol series [6].

In an acid hydrolyzate of saponin D by means of GLC of the aldonitriles of the sugars we identified glucose and rhamnose in a ratio of 1:1. The products of the methylation of glycoside D were shown by GLC, TLC, and mass spectrometry [7] to contain 2,3,4-tri-O-methyl-L-rhamnose, 2,3,4,6-tetra-O-methyl-D-glucose, and 3,6-di-O-methyl-D-glucose.

Enzymatic hydrolysis with the  $\beta$ -glucosidase from *Helix pomatia* of substance D led to the formation of dioscin as the sole product, and hydrolysis with an enzyme complex that we isolated from *Aspergillus niger* [8] gave trillin, as well. The enzymatic hydrolysis of saponin E with  $\beta$ -glucosidase gave gracillin, and hydrolysis with the enzyme complex again gave trillin as well.

As a result of the oxidative cleavage of glycoside D by the method of Tschesche et al., [9] we obtained a  $\Delta^{5,16}$ -pregnenolone glycoside and the lactone of  $\delta$ -hydroxy- $\gamma$ -methylvaleric acid, the constants of which corresponded to those given in the literature [10].

On the basis of the facts given above, the agreement of chromatographic mobilities with those of markers, and the identity of the constants, it may be concluded that glycosides D and E are protodioscin [6] and kikuba saponin [11], respectively.

In the combined steroid glycosides of *Tribulus terrestris* L. that we investigated, which posses an antiatherosclerotic action [12], the main components were bisdesmoside water-soluble tetraglycosides of the furastanol series ( $\approx 75\%$ ). We observed that in the fresh plant material the bisdesmosides were present in overwhelming amount (90%), while on drying the amount of monodesmosides increased. These results are also in good agreement with those given in the literature [13].

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