On the basis of the results obtained, the following provisional formula is proposed for the chalcone: 3',4',6',8',3,4-hexahydroxychalcone 2'-glucoside. The arrangement of the hydroxy groups is given by analogy with gossypetin.

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THE STRUCTURE OF SECURIGENIN AND SECURIGENOL

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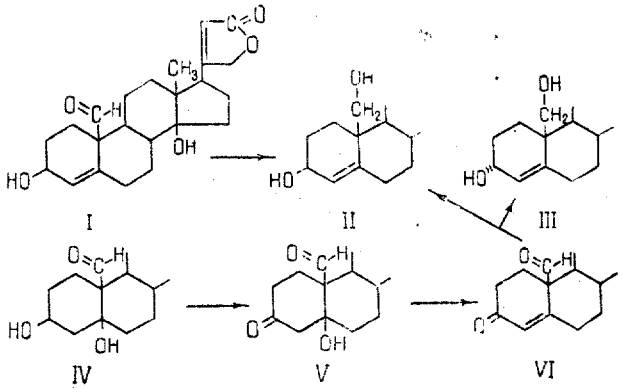
The isolation from Securigera securidaca (L.) of a new cardiac aglycone securigenin has been reported previously [1]. A further study of its structure has revealed new facts not compatible with the provisional formula proposed earlier [2].

Securigenin (I), $C_{23}H_{30}O_5$, has been shown by UV and IR spectroscopy to contain a butenolide ring, an aldehyde group, two hydroxy groups, and an isolated double bond in the nucleus. Securigenol, $C_{23}H_{32}O_5$, with mp 213-218° C, $[\alpha]_D^{22}$ +27.3° (c 1.01; methanol), with a maximum in the UV spectrum at 216 mμ (log ε 4.20) and a shoulder at 270-283 mμ (log ε 1.51-1.25) was obtained by the reduction of securigenin at the aldehyde group.

We have turned our attention to the high extinction of the aldehyde group in the UV spectrum of the aglycone ($\lambda_{max}^{C_2H_5OH}$ 308 mμ, log ε 2.19). This could be due to the homoconjugation of this group with the double bond. Several such positions of the double bond can be permitted in securigenin. By comparing the increment $[M]_D$ for various positions of the double bond in the steroids [3] we came to the conclusion that the double bond in securigenin is most probably in the Δ^4 position. To confirm this assumption Δ^4-strophanthidol was obtained. As is known, the directed formation of Δ^4 bond in the cardiac aglycones is possible only when a keto group is present at C_3 [4]. Usually, when an OH group at C_5 is split out, Δ^5 and $\Delta^{5,14}$ compounds are produced [5]. In 3-oxostrophanthidin (V), obtained by the selective oxidation of strophanthidin (IV) with oxygen in the presence of a Pt catalyst, the OH group at C_5 is readily split off in an acetic acid medium with the formation of 3-oxo-Δ^4-strophanthidin (VI). The reduction of this compound with $NaBH_4$ gave a mixture of products: 3α-hydroxy- and 3β-hydroxy-Δ^4-strophanthidols (III and II, respectively). By separating the mixture on a column of Al_2O_3 both products were isolated in the individual crystalline state. 3β-Hydroxy-Δ^4-strophanthidol (II) proved to be identical with securigenol.



A double bond at Δ^4 (securigenin) and Δ^5 (pachygenin [6]) imparts a number of characteristic features to the properties of aglycones having a carbonyl group at C_{10}: 1) the Δ^4 bond, in contrast to the Δ^5 bond, gives steroids a high positive rotation; 2) the optical rotatory dispersion spectrum has a positive Cotton effect in securigenin and a negative effect in pachygenin; 3) under mild conditions pachygenin readily forms a methylal and a semiacetal [7], while securigenin does not give these derivatives under the same conditions. This fact can probably be explained both by the

spatial remoteness of the OH group at C_3 of securigenin from the aldehyde group at C_{10} that is characteristic for aglycones of the cis-A/B series and also by the stability of ring A due to the presence of a double bond in it. Pachygenin, with a spatial arrangement of the A/B rings close to trans, like corotoxigenin [8], readily give the semiacetal form, which is favored by the ready transition of ring A into the boat form.

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CONFIGURATION OF SECURIGENIN AND SECURIGENOL

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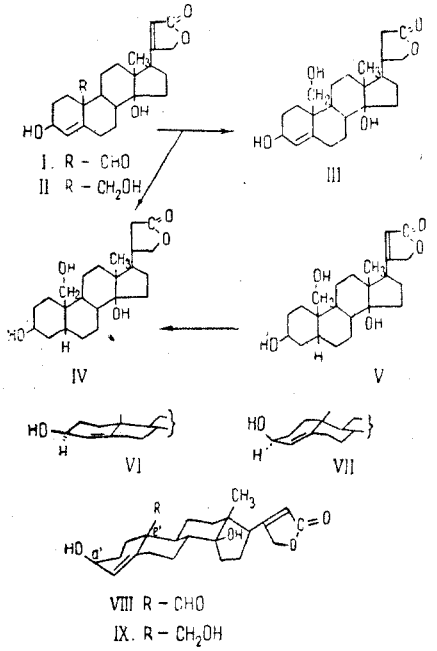
The NMR spectrum of securigenin acetate [1] is similar in its main features to the spectra of other cardenolides [2] and differs from the spectrum of strophanthidin acetate [3] only by a signal at 5.59 ppm, which we ascribe to the proton at Δ^4.

The presence of a double bond in ring A imparts a number of special features to the conformation of the molecule of securigenin (I). The difficulty in the formation of a methylal and a semiacetal gives grounds for assuming the presence in the aglycone of a linkage of rings A and B close to the cis form.



The hydrogenation of securigenol (II) over a Pd catalyst [4] did not give satisfactory results. The hydrogenation of securigenol over a more active Pt catalyst [5] in anhydrous methanol gave two products which did not give a positive