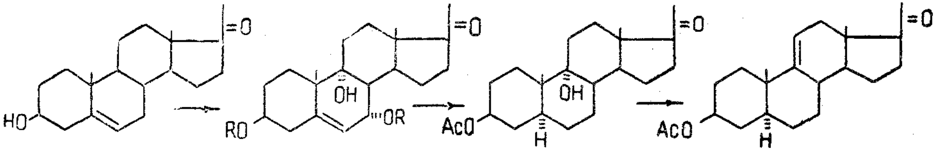
($\Delta[M]_D$ − 81.9°) and that between their acetate ($\Delta[M]_D$ − 499.0°) shows the α-configuration of the hydroxyl at C_7. Consequently, compound II is 3β,7α,9α-trihydroxypregn-5-en-20-one.



I

II R = H

III R = Ac

IV

V

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A CHALCONE FROM COTTON PLANT FLOWERS

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In a study of the flowers of the cotton plant of the thin-fibered type 5094I growing in the south of Uzbekhistan we have isolated a chalcone glycoside with the composition $C_{21}H_{21}O_{13}$.

The chalcone crystallizes from aqueous ethanol in two forms: with mp 202–203° C (decomp.) and with mp 228–229° C (decomp). The substance apparently has cis and trans forms.

On a paper chromatogram in the butan-1-ol—acetic acid—water (4 : 1 : 5) system a single clear spot with R_f 0.22 is found. The two forms give identical UV spectra with additives: λ_{max}, mμ, 385, 248, 260 (C_2H_5OH); 395, 265, (+CH_3COONa); 395, 265 (+H_3BO_3); 443, 270 ($AlCl_3$).

The complete splitting off of the sugar from the aglycone was achieved by heating the substance with concentrated hydrochloric acid in the boiling water bath for 10 min. This gave 65.4% of aglycone and 35.4% of glucose (1 : 1).

The aglycone, with the composition $C_{15}H_{11}O_8$, mp 308–309° C (decomp.), R_f 0.43 (BAW), crystallizes in the form of orange needles with a green tinge. When a paper chromatogram is sprayed with a 2% solution of sodium bicarbonate, the spot of the aglycone is colored dirty green.

UV spectrum of the aglycone with additives, λ_{max}, mμ, 380, 277, 260 (C_2H_5OH); 395, 270 mμ (+CH_3COONa); 390, 270 mμ (+H_3BO_3); 440, 270 mμ ($AlCl_3$).

The following derivatives were obtained: pentaacetal derivative $C_{29}H_{25}O_{15}$, mp 226–227° C (reaction with $AlCl_3$ negative); pentamethyl ether $C_{22}H_{25}O_8$ with mp 166° C (reaction with $AlCl_3$ negative).

The sugar formed after acid and enzymatic (Aspergyllus oryzae) hydrolyzes was identified as glucose by paper chromatography in the ethyl acetate—pyridine—water (2 : 1 : 2) system.

Qualitative reactions for a glucoside: no coloration with Mg and HCl and with Zn and HCl; brown-green coloration ethanolic $FeCl_3$ solution; dark red solution with a green fluorescence with concentrated H_2SO_4; red-orange solution with concentrated aqueous sodium hydroxide; bright yellow coloration with aqueous $SbCl_3$ solution. On paper chromatography, in ordinary light the spot was yellow and in UV light it was dark brown.

The properties of the chalcone glycoside are close to those of gossypin and gossypitrin and its aglycone is similar to the gossypetin previously isolated from the flowers of the cotton plant [1–3].

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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UDC 547.92+615.711.5

THE STRUCTURE OF SECURIGENIN AND SECURIGENOL

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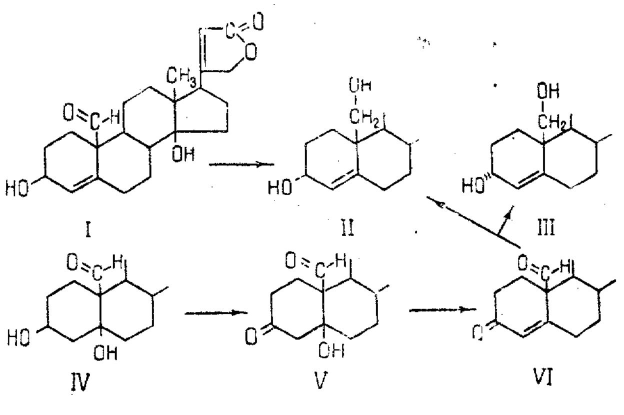
The isolation from Securigera securidaca (L.) of a new cardiac aglycone securigenin has been reported previously [1]. A further study of its structure has revealed new facts not compatible with the provisional formula proposed earlier [2].

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