Selective demethylation in position 3 has been recorded for a number of flavones [7]. Veratric acid and acetoveratrone were isolated from the products of the alkaline decomposition of the flavone. The hypsochromic shift observed on methylation is characteristic for flavones having a free hydroxy group in position 5 [6].

The spectra of the substance from the plant and its aluminum complex showed the bathochromic displacement characteristic for them [8]. When the UV spectra taken in an alcoholic solution and in sodium ethoxide solution were compared a characteristic shift was again observed [9].

Thus, we have established the identity of the compound isolated as 5-hydroxy-6, 7, 8, 3', 4'-pentamethoxyflavone (5-O-desmethylnobiletin).

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SYNTHESIS OF A MERCAPTOETHYL ETHER OF DEXTRAN

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The synthesis of physiologically active derivatives of dextran is arousing great interest [1–4], particularly derivatives of dextran containing mercapto groups. It is known that low molecular weight compounds including a mercapto group have a favorable action in the treatment of disturbances of the connection between respiration and the formation of adenosine triphosphate [5].

The dextran ether was synthesized by treating dextran with ethylene sulfide. 15 g of dextran was dissolved in 45 ml of 18% caustic soda, precipitated with methanol, dried, and treated, with stirring, with 300 ml of ethylene sulfide at 20° C for 4 hr, after which the precipitate was filtered off, washed with benzene, and dried.

In the reaction of dextran with ethylene sulfide there is the possibility of the simultaneous formation of the mercaptoethyl ether and of a graft copolymer of dextran and poly(ethylene sulfide), while the thiol groups of the alkyl residues and the graft chains may be oxidized in the air with the appearance of disulfide bonds. The product of the reaction contained 32% of sulfur and only 0.2% of thiol groups. Thus, under the conditions for synthesis used the oxidation of the thiol groups of the alkyl residues and the graft chains takes place almost completely.

To reduce the disulfide bonds, the products were treated with 250 ml of 5% hydrosulfite at 20° C for 24 hr. An insoluble copolymer of dextran and poly(ethylene sulfide) containing 38% of sulfur and practically free from thiol groups was separated by filtration. The copolymer was found to contain 30% of dextran and 70% of poly(ethylene sulfide). In view of the fact that in the graft copolymer the thiol groups are present only at the ends of the graft chains, it may be concluded that the molecular weight of the graft chains of the poly(ethylene sulfide) is very high.

The filtrate was acidified with hydrochloric acid, and methanol then precipitated a water-soluble derivative of dextran which was purified by pouring an aqueous solution into methanol. To characterize the composition of the product obtained, the total content of sulfur was found and the electrical exchange capacity was determined by the iodometric method. The product contained 20% of sulfur and the electrical exchange capacity was 6.2 mg-eq/g. At this value of the exchange capacity, the sample should contain 20.4% of thiol groups, i.e. practically all the sulfur atoms should be present as thiol groups, and the sample synthesized was a mercaptoethyl ether of dextran with a γ value of 165, which corresponds to the formula

$$[C_6H_7O_2(OH)_{1.35}(OCH_2CH_2SNa)_{1.65}]_n.$$

The amount of graft copolymer of dextran and poly(ethylene sulfide) isolated was about 50% of the weight of mercaptoethyl ether of dextran obtained.

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A CHEMICAL STUDY OF THE STRUCTURE OF SECURIGENIN AND ITS BIOSIDE SECURIDASIDE

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Securigenin, with the composition $C_{23}H_{32}O_6$, mp 234°–236°C, $[\alpha]^{20}_{D}$ +82° (in methanol), is the aglycone of securidaside, a cardiac glycoside isolated from the seeds of Securigera securidasa [1]. The aglycone has been found to contain an unsaturated lactone ring, an angular aldehyde group [2], and three hydroxy groups, one of which, at C_3, undergoes acetylation giving a monoacetate $C_{25}H_{34}O_7$ with mp 210°–214°C, $[\alpha]^{22}_{D}$ +40° (in methanol).

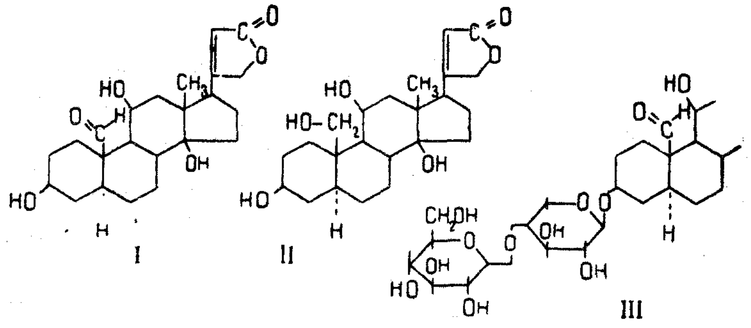
In an alkaline medium, the aglycone is converted into an iso compound giving a monoacetyl derivative $C_{25}H_{34}O_7$ with mp 197°–200°C, $[\alpha]^{22}_{D}$ +29.7° (in methanol), which excludes the presence of a hydroxyl in positions 12 and 16 and, in addition, confirms the β position of a butenolide ring and the presence of a hydroxyl in the 14β position. By oxidizing the acetate of the aglycone with chromic acid we obtained a neutral product with a yield of 95%. It is possible that the carboxy group which appears reacts immediately with a neighboring hydroxyl on C_1 or C_{11}, forming a lactone.

It is known that the acetylation of a hydroxyl in position 1 takes place in two weeks under severe conditions [3]. However, securigenin is not completely acetylated at position 3 in 12 hr, and undergoes no change on further acetylation. This fact permits the assumption that it contains a hydroxyl in position 11. It has been established that a hydroxyl in the 11α position readily undergoes acetylation [4], but securigenin acetylates only at position 3. Consequently, the third hydroxyl must be present in the 11β position.

For an additional proof of the presence of a hydroxyl in the 11β position, securigenin was reduced with sodium borohydride to securigenol (II), the properties of which are similar to those of panogenin, which has been isolated by Reichstein et al., [5]. Securigenol has the composition $C_{23}H_{34}O_6$, mp 215°–226°C, $[\alpha]^{22}_{D}$ + 17.3° (in methanol), and on acetylation it gave a diacetyl derivative whose oxidation with chromic acid gave a new product with a yield of 90% containing a keto group in position 11. The presence of a keto group at C_{11} was shown by the IR spectrum with absorption at 1675 cm^{-1}, which is characteristic for a keto group at C_{11}, in steroids [6].

The trans linkage of rings A/B was confirmed by the optical rotatory dispersion spectrum. The dispersion curve had the shape characteristic of the trans-A/B series for cardenolides with an aldehyde group at C_{19} [7].

On this basis, it may be assumed that securigenin is 3β, 11β, 14β-trihydroxy-19-oxo-5α-card-20(22)-enolide (I).



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