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

V. V. Zatula, N. V. Chernobrovaya, and D. G. Kolesnikov

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Securigenin, with the composition $C_{23}H_{32}O_6$, mp 234°–236°C, $[\alpha]_D^{20}$ +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, $[\alpha]_D^{22}$ +40° (in methanol).

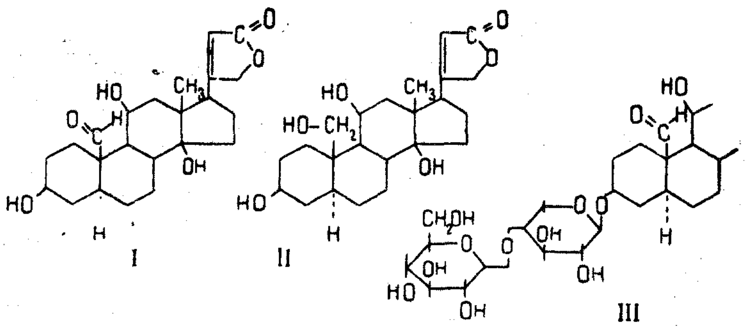
In an alkaline medium, the aglycone is converted into an iso compound giving a monoacetyl derivative $C_{25}H_{34}O_7$ with mp 197°–200°C, $[\alpha]_D^{22}$ +29.7° (in methanol), which excludes the presence of a hydroxyl in positions 12 and 16 and, in addition, confirms the β position of a butenolide 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, $[\alpha]_D^{22}$ + 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).


I II III

This structural formula was proposed by Lin Yung-lung and P. M. Loskarev for canescegenin [8, 9]. However, when the optical rotatory dispersion spectrum of canescein was taken it was found that it had the curved shape characteristic for the cis linkage or rings A and B. Consequently, we consider that the formula of canescegenin must be revised.

Securidaside, a bioside of securigenin, must have the structure of 3β-[β-D-xylopyranosyl-(4-1)-β-D-glucopyranosido]-11β, 14β-dihydroxy-19-oxo-5α-card-20(22)-enolide (III). The order of addition of the sugars was established by stepwise enzymatic hydrolysis [10]. The position of attachment of D-glucose to D-xylose was shown by the exhaustive methylation of securidaside with dimethyl sulfate in an alkaline medium and subsequent methanolysis and hydrolysis. The methylated sugar derivatives obtained were isolated in the individual state and identified with samples of 2, 3-di-O-methyl-D-xylose and 2, 3, 4, 6-tetra-O-methyl-D-xylose, which shows the pyranose forms of both monosaccharides and a 1-4 bond.

The sample of canescein was kindly given to us by Lin Yung-lung and the samples of methylated sugars were supplied by N. I. Kuibina and Yu. P. Solov'eva.

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Khar'kov Chemical and Pharmaceutical Scientific Research Institute

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CARDIAC GLYCOSIDES OF THE SEEDS OF EVONYMUS EUROPAEA

S. G. Kislichenko, I. F. Makarevich, and D. G. Kolesnikov

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According to Zoz (cited in [1]), E. medirossica Klok. is one of the geographical races, distributed in the territory of the European part of the USSR, of E. europeae auct.

We have shown by paper chromatography that the seeds of this plant contain not less than eight cardenolides, which have been provisionally denoted by the symbols SK-1, ... SK-8. SK-1 and SK-4 have been obtained in the individual crystalline state. For this purpose, the comminuted seeds were subjected to the action of an enzyme preparation from the fungus Aspergillus oryzae at 42°-45° C for three days. The glycosides were extracted with 70% alcohol and the extracts were evaporated in vacuo to give aqueous residues. The cardenolides SK-4, SK-3, SK-2, and, in part, SK-1 were extracted with chloroform, and SK-1 and SK-5 with a mixture of alcohol and chloroform (1:2). The chloroform and alcohol–chloroform extracts were evaporated separately and the residues were chromatographed on columns of alumina. The cardenolide SK-4 was eluted with chloroform–alcohol (97:3) and was crystallized from methanol, and the glycoside SK-1 with alcohol–chloroform (1:3) and was crystallized from moist acetone (table).

Substance	Empirical formula	Mp, °C	$[\alpha]_D$, deg	Coloration with conc. H_2SO_4
SK-4 (evomonoside)	$C_{29}H_{44}O_8$	244–246	–26.47 (in methanol)	Brown → red purple → purple
SK-1	$C_{29}H_{44}O_9$	158–160	–20.03 (in methanol)	Yellow → pink → → purple
Aglycone from SK-4 (digitoxigenin)	$C_{28}H_{34}O_4$	244–248	+17.80 (in chloroform)	Yellow → yellow orange → pale blue
Monosaccharide from SK-4 (L-rhamnose)	—	83–100		—