

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 of 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 3 β -[β -D-xylopyranosyl-(4-1)- β -D-glucopyranosido]-11 β , 14 β -dihydroxy-19-oxo-5 α -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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CARDIAC GLYCOSIDES OF THE SEEDS OF EVONYMUS EUROPAEA

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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. europaea 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 ₂ SO 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	—	—

SK-4, from its properties and hydrolysis products, was identified as evomonoside, which has been obtained previously by Reichstein et al. [2-4].

SK-1 proved to be a monoglycoside with a fairly high biological activity (10 370 cat units). The properties presented give reasons for assuming that this is a new cardiac glycoside.

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A CASE OF THE SPONTANEOUS FORMATION OF HYDROCHLORIDES IN CRUDE MIXTURES OF ALKALOIDS

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When mixtures of alkaloids from various samples of *Anabasis aphylla* [1] were stored for two weeks, in a number of cases a crystalline deposit was formed, the hydrochloride of one of the components of the mixture isolated (anabasine, isoanabasine [2], or lupinine). The reason for the appearance of a hydrochloride may be the partial decomposition of the chloroform in the alkaline medium, since on extraction with ether no precipitate has been found. It has been shown that isoanabasine forms a hydrochloride more readily than anabasine. Below we give the amounts of the mixture of alkaloids and bases isolated from the hydrochloride (% by weight of the dry plant).

<u>Total</u>	<u>Base isolated from a hydrochloride</u>	<u>Nature of the precipitate</u>
2.60	—	—*
4.30	0.12	Isoanabasine
2.20	—	—*
9.50	0.73	Lupinine
3.15	0.056	Isoanabasine
5.70	—	—*
4.00	0.41	Lupinine
		Anabasine
		Isoanabasine
5.20	0.79	Lupinine

* No precipitate was formed.

** Lupinine, 0.082%; anabasine, 0.34%; and isoanabasine, 0.06%.

The plant was extracted with 5% acetic acid. The acid extract was made alkaline with a 40% solution of caustic soda and was exhaustively extracted with chloroform. Twelve hours after the solvent had been distilled off, a precipitate of hydrochloride formed which was triturated with ether, filtered, recrystallized from acetone, and converted into the base. Lupinine was identified by a mixed melting point test. Anabasine and isoanabasine were converted into the methiodides of the benzoyl derivatives and their melting points were determined.

From anabasine hydrochloride was obtained a previously unreported complex salt, anabasine chloride tartrate, with mp 163° C.

Found, %: C 52.37, 52.53; H 6.41, 6.56; N 10.51, 10.77; Cl 12.46. Calculated for $2C_{10}H_{14}N_2 \cdot C_4H_6O_6 \cdot 2HCl$, %: C 52.67; H 6.77; N 10.23; Cl 12.80.

The anabasine isolated after the decomposition of this salt had $[\alpha]_D -78^\circ$ (c 1.1235; benzene).