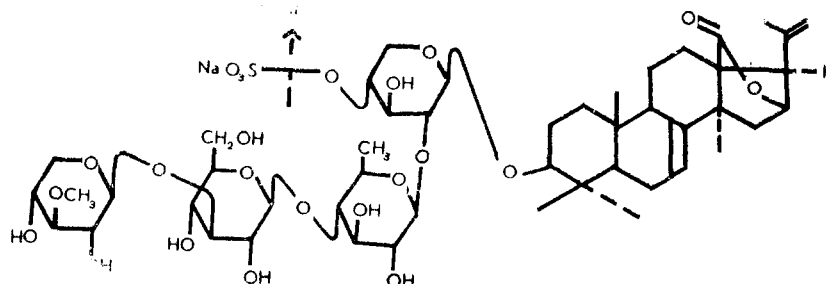


CUCUMARIOSIDE G<sub>2</sub> - A MINOR TRITERPENEGLYCOSIDE FROM THE HOLOTHURIAN*Eupentacta fraudatrix*S. A. Avilov, V. I. Kalinin, A. I. Kalinovskii  
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From the total triterpene glycosides of the holothurian *Eupentacta fraudatrix* [1] with the aid of HPLC (Zorbax-ODS, 4.8 × 250 ml, water-acetone (73:27), 1 ml/min) we have isolated a minor glycosidic component which we have called cucumarioside G<sub>2</sub> (I), mp 234-235°C,  $[\alpha]_D^{20} - 46^\circ$  (c 0.1; pyridine).



A comparison of the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of cucumarioside G<sub>2</sub> and its desulfated derivative (II), mp 190-192°C,  $[\alpha]_D^{20} - 74^\circ$  (c 0.1; pyridine) with the spectrum of cucumarioside G<sub>1</sub> [1], a monosaccharide analysis, and the results of analytical Smith degradation under the conditions described in [2] unambiguously showed the complete identity of the carbohydrate components in compound (I) and in the previously known cucumarioside G<sub>1</sub> [1].

The structure of the aglycone moiety of (I) was established by comparing its  $^{13}\text{C}$  spectra with the spectrum of psolusoside B from the holothurian *Psolus fabricii*, the aglycone of which is 20(S)-acetoxy-3 $\beta$ -hydroxy-18,16-diene-18,16-carbolactone [3, 4]. The C-1-C-19, C-30, C-31, and C-32 signals in the spectra of (I) and psolusoside B are close or coincide, which indicates the identity of the structures of the polycyclic fragments of the aglycons in these glycosides. This fragment, both in (I) and in psolusoside B, is substituted at C-17.

This conclusion was confirmed by the  $^1\text{H}$  NMR spectra of derivative (II), which contained signals at 5.63 m (H-7), 3.00 dm (H-9), 1.98 dd (H-15 $\alpha$ ), 2.16 dd (H-15 $\beta$ ), 4.75 d (H-16), 2.99 s (H-17), 1.03, 1.16 s, 1.34 s (6H) (CH<sub>3</sub>-19, 30, 31, 32). Also in favor of the presence of an 18,16-carbolactone in the cyclic system of the aglycone moiety of (I) is the zero value of the spin-spin coupling constant between H-17 and H-16 [3]. Furthermore, in the  $^{13}\text{C}$  NMR spectrum of (I) there are three signals of carbon atoms not belonging to the polycyclic system:

TABLE 1.  $^{13}\text{C}$  NMR Spectrum of the Aglycone Moiety of Glycoside (I) (C<sub>5</sub>D<sub>5</sub>N)

Atom	ppm	Atom	ppm	Atom	ppm	Atom	ppm	Atom	ppm
C-1	35,8	C-6	23,4	C-11	23,0	C-16	80,4	C-21	21,8
C-2	27,0	C-7	*	C-12	20,0	C-17	59,1	C-22	113,8
C-3	88,8	C-8	147,3	C-13	56,7	C-18	180,3	C-30	17,2
C-4	35,5	C-9	46,5	C-14	46,0	C-19	23,9	C-31	28,6
C-5	47,3	C-10	35,5	C-15	41,0	C-20	139,7	C-32	34,0

\*The signal coincides with a signal of the solvent.

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at 139.7 and 113.8 ppm, and also at 21.8 ppm, relating to an isopropenyl fragment. The presence of such a group was also confirmed by the  $^1\text{H}$  NMR spectrum (1.74 ppm, s ( $\text{CH}_3$ -21) and 5.07 and 4.98 ppm, both br.s (2 H-22)). Since all the signals of the carbohydrate chain and the  $^{13}\text{C}$  NMR spectrum of glycoside (I) coincided those for the previously known cucumarioside  $\text{G}_1$  while the number of signals for the aglycon moiety of (I) corresponded to 25 carbon atoms, we assume that the isopropenyl fragment in the aglycon of glycoside (I) is attached to C-17.

Thus, the minor component from the glycosidic fraction of the holothurian Eupentacta fraudatrix, cucumarioside  $\text{G}_2$ , is 3 $\beta$ -hydroxy-23,24,25,26,27-pentanorlanosta-7,20(22)-diene-18,16-carbolactone 3-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 4)-O- $\beta$ -D-quinovopyranosyl-(1 $\rightarrow$ 2)-(4-O-(sodium sulfato)- $\beta$ -D-xylopyranoside. This is the first time that a glycoside with an 18,16-carbolactone group and a shortened side chain in the aglycon has been isolated from holothurians. Consequently, it is a representative of a new structural type of holothurian glycosides.

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#### ALKALOIDS OF *Corydalis caucasica*

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Continuing investigations of alkaloids of plants of the genus Corydalis [1, 2] of the flora of the Northern Caucasus, we have studied the alkaloid composition of the epigeal part of Caucasian corydalis Corydalis caucasica D.C. gathered in the region of Pyatigorsk (Stavropol'krai).

Alkaloids have been isolated previously from Caucasian corydalis: chelerythrine, sanguinarine, protopine, allocryptopine and bulbocapnine [2].

By chloroform extraction, from the epigeal part of Caucasian corydalis gathered in the flowering period we have isolated 0.85% of alkaloids and separated them into phenolic and nonphenolic fractions. Column chromatography of the nonphenolic fraction with elution by chloroform-ethanol in various ratios of the nonphenolic fraction enabled us to isolate stylopine, adluminidine, d- $\beta$ -hydrastine, d-bicuculine, protopine and alloprotopine, and that of the phenolic fraction scoulerine, bulbocapnine, isoboldine, cheilanthifoline, N-methylaurotetane, and norisocorydine. All the alkaloids isolated were identified on the basis of physicochemical properties and spectral characteristics and also from the absence of depressions of the melting point of mixtures [3-6].

The main alkaloids were stylopine and adluminidine, and also protopine, d-bicuculine, and allocryptopine.

Thus, the alkaloids scoulerine, d-bicuculine, d- $\beta$ -hydrastine, adluminidine, cheilanthifoline, N-methylaurotetanine, and isoboldine have been isolated from this plant for the first time.

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