1,1,4,5-Tetramethylcycloheptane (IV), which has not been described in the literature previously, had: d_4^{20} 0.8037, n_D^{20} 1.4435; for $C_{11}H_{22}$, found, %: C 85.74, H 14.26; calculated, %: C 85.72, H 14.28. IR spectrum (cm^{-1}): 765, 788, 818, 856, 881, 955, 987, 995, 1057 – the skeletal vibrations of a cycloheptane ring; and 1142, 1181, 1378, 1385 – the vibrations of a geminal $2CH_3$ group. PMR spectrum (δ, ppm): 0.84 (s (2 H, gem-$(CH_3)_2$); 0.85 t (J = 57 Hz, 6 H, 2 CH_3); 1.18-1.5 m (8 H, 4 CH_2); 1.50-1.83 m (2 H, 2 CH). The properties of (V) and (VI) corresponded to those given in the literature [3, 4].

The presence of (IV) as the main component gives grounds for assuming that on the catalyst the dehydration of (III) takes place with the formation of 4-methylene-2-carene (VIII), which isomerizes under the reaction conditions into 4-methylcara-2,4-diene (IX). Compound (IX) is present in equilibrium with its tautomer – 3,4,7,7-tetramethylcyclohepta-1,3,5-triene (X) [2], the hydrogenation of which gives (IV). The formation of (VI) is due to the isomerization of (X). The presence of (V) in the hydrogenate confirms the participation of (VIII) as an intermediate in the reaction. The formation of (VII) is explained by the esterification of (III) by acetic acid under the reaction conditions.

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TWO-STAGE SMITH DEGRADATION OF HOLOTHURIN B_1 FROM THE HOLOTHURIAN *Holothuria floridana*

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We have previously established that the native aglycone of holothurian B_1 from the Caribbean holothurian *Holothuria floridana*, holost-9(11)-ene-3β,12α,17α-triol, can be obtained in small amounts by the acid hydrolysis of the glycoside. However, the bulk of the mixture of aglycones formed in this process consists of artifactual genins [1]. The demand for the native aglycones of triterpene glycosides for biosynthetic and biochemical investigations makes it necessary to seek directed approaches to their production. Recently, in our laboratory, the possibility has been shown of using the method of two-stage Smith degradation for obtaining the native aglycones of the hexaosides of the holothurian *Bohadschia argus* [2]. We have used this method to obtain the native genin of a sulfated triterpene bioside – holothurin B_1 from the holothurian *H. floridana* [3]. As a result, we have for the first time isolated and characterized two progenins of holothurian B_1 – 3β-[4-(sodium sulfato)-β-D-xylopyranosyloxy]holost-9(11)-ene-12α,17α-diol (I) and 3β-D-xylopyranosyloxyholost-9(11)-ene-12α,17α-diol (II) – and also the native aglycone (III) of holothurin B_1 (Fig. 1).

The Smith cleavage of holothurin B_1 was carried out by the usual method [4]. The mixture of progenins (I) and (II) obtained after mild acid hydrolysis (0.5 N HCl, 22°C, 1.5 h) of the periodate-oxidized and (sodium tetrahydroborate)-reduced holothurin B_1 was separated on silica gel in the chloroform–methanol–water (75:25:2) system. Progenin (I) had mp 246-248°C (from ethanol), $[\alpha]_D^{20}$ −13.95° (c 0.18; pyridine) and progenin (II) mp 227-230°C (from ethanol), $[\alpha]_D^{20}$ −10° (c 0.324; pyridine). After a second Smith cleavage of progenin (II), the aglycone (III) was isolated with mp 237°C, $[\alpha]_D^{20}$ +1.04° (c 0.24; chloroform). The ^1H NMR spectrum of aglycone (III) was identical with that of the native genin of holothurin B_1 [1]. The positions of the signals of the C-9, C-11, and C-12 atoms in the ^{13}C NMR spectra of (I), (II), and (III) (Table 1) show the presence of a 12α-hydroxy-9(11)-ene fragment, which is characteristic for the initial glycoside [3], in each of the compounds isolated. The differences in the positions of the signals of the carbon atoms of the carbohydrate chains of the progenins show that progenin (II) differs from (I) by the absence of a sulfate group at C-4

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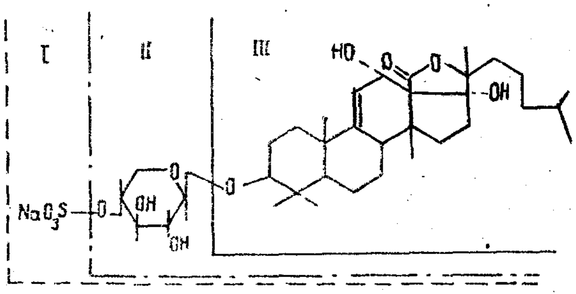

Fig. 1. Structures of progenins (I) and (II) and of the native aglycone (III) of holothurin B_1 from the holothurian *H. floridana*.

TABLE 1. Characteristics of the ^{13}C NMR Spectra of Compounds (I), (II), and (III) (Brüker HX-90E, ppm, TMS — 0)

C atom	Compound			C atom	Compound		
	I	II	III		I	II	III
C-1	36,6	36,40	36,4	C-19	22,7	22,6	22.68
C-2	26,7	27,1	27,7	C-20	87,0	87,15	87.20
C-3	88,5	88,6	78,6	C-21	22,99	22,23	22.68
C-4	39,9	39,75	39,8	C-22	36.45	36,5	36,2
C-5	52.83	52,8	52,2	C-23	22,19	22,2	22,1
C-6	21.25	20,6	20,9	C-24	36,5	39,5	39,2
C-7	27,96	28,01	28,3	C-25	28,3	28,3	28,4
C-8	40.94	40,9	40,55	C-26	22,6	22,67	22,6
C-9	153,9	154,02	156,35	C-27	22,65	22,7	22.6
C-10	39,76	39,7	39,5	C-30	16,9	16,96	15.6
C-11	115,5	115,5	113,6	C-31	28.2	28,3	28,3
C-12	71,5	71,6	71.9	C-32	20,3	20,01	20,0
C-13	58,7	58,6	58.6	C′-1	106.9	107,6	
C-14	46,4	46,34	46,75	C′-2	76,7	75,4	
C-15	38,88	38,9	38.3	C′-3	76,6	78,4	
C-16	36.3	36,2	36.1	C′-4	75,3	71,16	
C-17	89,3	89.3	89,0	C′-5	64,7	67,06	
C-18	174,5	174,68	174,3				

of the xylose residue [3]. The yield of aglycone was 11.6% calculated on the initial glycoside.

Thus, the two-stage Smith degradation of sulfated triterpene glycosides can be used to obtain progenins and native aglycones.

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