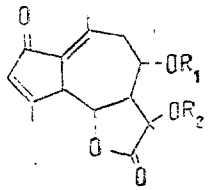
The value of the H-8 chemical shift (5.52 ppm) shows that an unsaturated aliphatic acid, in this case senecioic acid, is present at C-8 [2]. In the 2.04 ppm region there is the superposition of the signals of a vinylmethyl group at C-19 and of the methyl group of an acetic acid residue. On the basis of the facts given above, the structure of 11-acetoxy-2-oxo-8-senecioyloxy-guaia-3,10-dien-6,12-olide is justified for ferolide.



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TRANSFORMATIONS OF 4-HYDROXYMETHYL-2-CARENE UNDER THE CONDITIONS OF HETEROGENEOUS HYDROGENATION

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The main product of the hydrogenation of 2- and 3-carenes (I and II) in the liquid phase over Pt is carane [1]. The hydrogenation of the same terpenes over Pd leads to the formation of 1,1,4-trimethylcycloheptane [1]. It was assumed that the formation of compounds with a cycloheptane skeleton was connected with the occurrence of a reaction in which (I) was dehydrogenated to cara-2,4-diene with its subsequent tautomeric transformation into 3,7,7-trimethylcyclohepta-1,3,5-triene [2]. It is known that the liquid-phase hydrogenation over Pt of 4-hydroxymethyl-2-carene (III) — an oxygen-containing terpenoid with a bicyclic structure similar to that of (I) — gives 4-hydroxymethylcarane [3].

We now give the results of a study of the liquid-phase and gas-phase hydrogenation of (III) over palladized carbon (2% of Pd).

Liquid-phase hydrogenation was carried out at 20-80°C and atmospheric pressure in octane and glacial acetic acid for 24 h at a substrate:catalyst ratio of 10:1, and vapor-phase hydrogenation at 200-250°C in a catalytic apparatus in a current of H_2 with a time of contact of (III) and catalyst of 0.91-0.98 sec.

The composition of the hydrogenate was monitored by GLC.

When (III) was hydrogenated at 20°C no transformations whatever were observed. When the temperature was raised to 80°C in octane, a mixture of hydrocarbons (4%) consisting of 1,1,4,5-tetramethylcycloheptane (IV) (80%), 4-methylcarane (V) (15%), and 4-isopropyl-1,2-dimethylbenzene (VI) (5%) was formed. The hydrogenation of (III) in glacial acetic acid at 80°C led to the production of these hydrocarbons (7%) and the acetate of 4-hydroxymethyl-2-carene (VII) (36%). The properties of the (VII) isolated corresponded to those given in the literature [3].

In the vapor-phase hydrogenation of the (III) with its complete conversion, the hydrogenate contained (IV) (65-45%), (V) (14-9%), (VI) (18-30%), and an unidentified substance (3-16%) which could not be isolated because of its ready isomerization and which is presumed to be 4-isopropenyl-1,2-dimethylbenzene. The components of the hydrogenate were isolated by the PGLC method and were identified from their physicochemical properties and spectral characteristics.

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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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UDC 547.996:593.96

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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