THE STRUCTURES OF THE PRODUCT OF THE PARTIAL HYDROLYSIS OF POLYGONATOSIDES C^1 AND C^2 FROM THE RHIZOMES OF Polygonatum stenophyllum

L. I. Strigina, E. V. Kol'chuk,* and V. V. Isakov

UDC 547.917+547.918

Continuing an investigation of the structures of polygonatosides C^1 and C^2, which are glycosides of pennogenin [1], we have isolated the products of the partial acid hydrolysis (progenin I) and of the enzymatic hydrolysis (juice of the snail Eulota maackii progenins II and III) of a mixture of C^1 and C^2. From the similarity of its physical constants [mp 204-206°C, EtOH, $[\alpha]_D^{20}$ −53.7° ($CHCl_3$)] and the IR and NMR spectra of the corresponding acetates, progenin I was identified as pennogenin 3-O-α-D-glucopyranoside [2]. Using the method of noise decoupling and the results of previous work [3-5] we have for the first time made a complete assignment of the signals in the ^{13}C NMR spectrum of the acetate progenin I taken in $CDCl_3$ (standard – TMS) on a Bruker HX 90E instrument at a working frequency of 22.63 MHz, δ_C, ppm: C-21, 8.05, C-18, 17.09; C-27, 17.5; C-19, 19.36; C-11, $\underline{C}H_3CO$, 20.66×5; C-24, 28.20; C-2, 29.56 (δ_{C-2} acetate of I−pennogenin, -2.04); C-25, 30.08; C-15, 30.87; C-23, 31.26; C-8, C-12, 31.64×2; C-7, 32.40; C-10, 36.84; C-1, 37.40; C-4, 38.99 ($\Delta\delta_{C-4}$ acetate of I, pennogenin, -3.31); C-13, 43.80; C-20, 44.64; C-9, 49.78; C-14, 52.89; C'-6, 62.12; C-26, 66.80; C'-4, 68.62; C'-2, C'-5, 71.74×2 ($\delta_{C'-2}$ acetate of I−$Me(OAc)_4$-β-D-Glcp [5], +0,44); C'-3, 72.98; C-3, 79.99 ($\Delta\delta_{C-3}$ acetate of I−pennogenin, +8.39); C-17, 90.14; C-16, 90.98 C'-1, 99.75 ($\Delta\delta_{C'-1}$acetate of I −$Me(OAc)_4$-β-D-Glcp [5], -1.75); C-22, 110.08; C-6, 121.78; C-5, 140.43; $CH_3\underline{C}O$×4, 169.29, 170.20, 170.60. The values given in parentheses, showing the influence of glycosylation on the signals of the C atoms of the aglycone (δ_C) and of glucose ($\delta_{C'}$) correspond to figures given in the literature [5].

Thin-layer chromatographic analysis of the products of the enzymatic hydrolysis of the individual polygonatosides C^1 and C^2 showed that progenin (III) is formed from C^1 and C^2, and progenin II only from C^2. Progenin II, mp 247-251°C (EtOH), $[\alpha]_D^{20}$ −107.05° (EtOH). Progenin III ($[\alpha]_D^{20}$ −79.9°, EtOH) was characterized in the form of the acetate, mp 193.5-196°C (EtOH), $[\alpha]_D^{20}$ −48° (chloroform).

The qualitative and quantitative monosaccharide composition, determined by the GLC method on peracetates of the aldononitriles [6] showed that progenins II and III included glucose and rhamnose (1:1). The glycosylation shifts ($\Delta\delta_C$) in the ^{13}C NMR spectra of the acetates of progenins II and III were the same as for the acetate of progenin I.

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* Deceased.

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center of the Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 711-712, September-October, 1977. Original article submitted May 4, 1977.

0009-3130/77/1305-0597$07.50