REACTIONS OF PENNOGENIN AND RELATED COMPOUNDS.

I. PRODUCTION OF FULL ACETATES OF PENNOGENIN GLYCOSIDES

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UDC 547.918+547.92+543.422.25

The possibility of obtaining the full acetates of some glycosides of 25R-spirost-5-ene-3β,17α-diol (pennogenin, I) — the 3-O-β-D-glucopyranoside of (I) (II), the 3-O-[O-α-L-arabinofuranosyl-(1 → 4)][O-α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranoside of (I) (III), and the 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)][O-α-L-rhamnopyranosyl-(1 →4)]-β-D-glucopyranoside of (I) (IV — under conditions promoting the acetylation of the hindered 17α(OH) group of (I) [1] has been studied. Products of the reaction of (II), (III), and (IV) under the conditions given in (I) which were chromatographically homogeneous on TLC (SiO_2— $CaSO_4$) in the benzene—ethyl acetate (3:1) system — (V), (VI), and (VII), respectively [R_f (V) > R_f (VII) > R_f (VI)] — were studied by ^{13}C NMR spectroscopy (Bruker HX-90E spectrometer, 22.63 MHz). Analysis of the ^{13}C NMR spectra of (V), (VI), and (VII) showed that the ^{13}C chemical shifts (CSs) of their aglycone moieties were practically identical with those of the 3,17-di-O-acetate of (I), (VIII), with the exception of the signal due to the carbon atoms of ring A. ^{13}C NMR ($CDCl_3$) of (V), δ, ppm: 9,55 (C-21), 17.1 (C-27), 17.4 (C-18), 19.4 (C-19), 20.7 (C-11, $CH_3 \cdot CO \times 4$), 22.3 ($CH_3 \cdot CO$ at C-17), 28,4 (C-24), 29.5 (C-2), 30.2 (C-25), 31.5 (C-23), 31.9 (C-7, C-8)*, 32.2 (C-15)*, 33.0 (C-12)*, 36,8 (C-10), 37.2 (C-1), 38,9 (C-4), 46,1 (C-20), 46.3 (C-13), 49,7 (C-9), 53.5 (C-14), 62.2 (Glc C′-6), 66.9 (C-26), 68,6 (Glc C′-4), 71.6 (Glc C′-2), 71.7 (Glc C′-5), 73.0 (Glc C′-3), 80.0 (C-3), 82,3 (C-16), 99,7 (Glc C′-1), 101.4 (C-17), 108.0 (C-22), 122,0 (C-6), 140.2 (C-5), [169.4, 170,3×170.6 ($CH_3 \cdot COO$)].

Conversely, the ^{13}C CSs of the atoms of ring A and of the carbohydrate chains of (V), (VI), and (VII) were close to those of the acetates (II), (III), and (IV) containing a free C-17α(OH) group that we had obtained previously [2-4]. This shows that under the action of acetic anhydride in the presence of a catalytic amount of p-toluenesulfonic acid (stirring at room temperature for 7 h), the full acetates of (II), (III), and (IV) [(V), (VI), and (VII)] were formed. The acetylation of the C-17α(OH) group of the aglycone was not accompanied by the degradation of the carbohydrate chains during the reaction.

The ^{13}C NMR spectra were taken by V. V. Isakov.

LITERATURE CITED

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*The assignment may be interchanged.

Pacific Ocean Institute of Bioorganic Chemistry, Far-Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 127-128, January-February, 1985. Original article submitted July 9, 1984.

0009-3130/85/2101-0128$09.50