Progenin (VII), mp 268-269°C (ethanol), $[\alpha]_D^{20}$ −42.1° (c 0.5; pyridine).

SUMMARY

The complete structures of thelenotosides A and B obtained from the holothurian *T. ananas* have been established as 23(S)-acetoxy-3β-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-O-β-D-xylopyranosyl-(1→4)-O-β-D-quinovopyranosyl-(1→2)-β-D-xylopyranosyloxyl]holost-7-ene and 23(S)-acetoxy-3β-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-O-β-D-xylopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→2)-β-D-xylopyranoxyloxy]holost-7-ene, respectively.

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^{13}C NMR SPECTRA OF STEROID GLYCOSIDES.

II. ACETATES OF PENNOGENIN GLYCOSIDES

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The ^{13}C NMR spectra of two acetates of pennogenin glycosides have been measured and an assignment has been made of the signals of the C atoms. The mutual influence of the aglycone and the component carbohydrate chains on the chemical shifts of the signals of the corresponding C atoms has been determined.

^{13}C NMR spectroscopy is being used successfully in structural studies of steroid glycosides [1-6]. The ^{13}C NMR spectra of acetates of the glycosides are being used for a similar purpose to a smaller degree [7, 8]. However, the study of the possibility of obtaining structural information from the spectra of the acetates is of interest, since natural steroid glycosides are frequently separated in the form of the corresponding acetates.

We have previously made an assignment of the signals in the ^{13}C NMR spectrum of pennogenin β-D-glucopyranoside acetate (I) [7]. In the present paper we give information on the ^{13}C NMR spectra of two other pennogenin glycoside acetates: the acetates of the O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranoside (II) and of the O-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside (III), which we have isolated previously [7]. We also give the glycosidation shifts for the aglycone ($\Delta\delta = \delta_C$ for the glycoside acetate − δ_C for the aglycone) and for the acetylated monosaccharides (II) and (III) ($\Delta\delta = \delta_C$ of the glycoside acetate − δ_C of the methyl glycoside acetate), illustrating the mutual influence of the aglycone and the component carbohydrate chains.

The assignments of the C-2' and C-5' signals (δ 71.6 and 71.75 ppm, respectively) in the spectrum of (I) [7] have been refined by the method of selective decoupling from protons. The signals of the C atoms of the aglycone moieties of (II) and (III), with the exception of the signals of ring A, are identical with those of pennogenin [9]. The values of the chemi-

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TABLE 1. ^{13}C NMR Chemical Shifts (δ, ppm) and Glycosidation Shifts (Δδ, ppm) of the C Atoms of Ring A of the Aglycone and of the Carbohydrate Moieties of (II) and (III)

C atom	II		III	
	δ	Δδ	δ	Δδ
1	36,9	−0,4	36,9	−0,4
2	29,6	−2,0	29,6	−2,0
3	80.0	+8,4	79,2	+7,6
4	39,1	−3,2	38,4	−3,9
5	140.4	−0,5	140,2	−0,7
6	121,8	+0,5	122.05	+0.75
1′	99,5[a]	−2,0	99.6	−1,9
2′	72.3	+1,0	75.5	+4,2
3′	74.3	+1,4	74,9	+2,0
4′	77,4	+8,9	68,95	+0.45
5′	72,5	+0,7	71,7	−0,1
6′	62,3	+0,3	62,2	+0,2
1″ and 1‴	99,4[a]	+0,9	97,35	−1,15
2″ and 2‴	70.2[b]	+0,4	70,3	+0,4
3″ and 3‴	68,6	−0,6	68,7	−0,5
4″ and 4‴	70,8[b]	−0,2	71,4	+0,4
5″ and 5‴	67,9	+1,6	66,5	+0,2
6″ and 6‴	17,2	−0,2	17,3	−0,1

[a, b] Assignments within the vertical columns not unambiguous.

cal shifts of the signals of ring A of the aglycone and of the carbohydrate moieties of (II) and (III) and of the glycosidation shifts are given in Table 1.

A comparison of the spectra of (I), (II), and (III) revealed a dependence of the chemical shifts of the signals of the C atoms of ring A on the structure of the carbohydrate chain Thus, when the $(OAc)_3$-α-L-Rhap-(1→2) fragment (III) is present in the carbohydrate chain, C-3(α) and C-4(β) are more screened than in the case of the $(OAc)_3$-α-L-Rhap-(1→4) (II) and $(OAc)_4$-β-D-Glcp (I) fragments [7]. C-5 (γ) and C-6 (δ) undergo the influence to a smaller degree. The introduction of an additional carbohydrate unit has only a small influence on C-1 (γ).

In the spectrum of (II), the C-atoms of the $(OAc)_3$-glycosyl and $(OAc)_3$-rhamnosyl units resonate in different regions. The assignment of the signals of the C atoms of the carbohydrate moiety is based on the results for Me $(OAc)_4$-β-D-glucopyranoside [8] and Me $(OAc)_3$-α-L rhamnopyranoside [10] and was confirmed by selective decoupling from protons. The assignment of the signals of the C atoms of the $(OAc)_3$-β-D-glucopyranosyl unit in the spectrum of (III) differs from that reported previously for the acetate of a triterpene glycoside containing the O-$(OAc)_3$-α-Rhap-(1→4)-$(OAc)_3$-β-D-Glcp fragment [11]. In the spectrum of (III), the regions of the signals of the $(OAc)_3$-glucosyl and $(OAC)_3$-rhamnosyl units overlap one another. The assignment of the signals in the spectrum of (III) was performed by selective proton decoupling.

It can be seen from a comparison of the spectra of (II) and (III) that $(OAc)_3$-α-L-rhamnosyl units attached by (1→2) and (1→4) bonds differ greatly in the degree of screening of the C-1‴ and C-1″ atoms and the C-5‴ and C-″ atoms, and the α glycosidation shifts for the attached monosaccharides are opposite in sign. The difference mentioned may have diagnostic value for determining types of bonds.

EXPERIMENTAL

^{13}C NMR spectra were taken on a Bruker HX-90 E instrument in $CDCl_3$ at 30-32°C using concentrations of ≈5%. The accuracy of measurement was ±0.05 ppm. The acetates (I), (II), and (III) were obtained by the usual method from the corresponding glycosides [7].

SUMMARY

1. The mutual influence of the aglycone and of the acetylated monosaccharides forming the carbohydrate chains of two pennogenin glycoside acetates has been studied.

2. The $(OAc)_3$-α-L-Rhap-(1→2) fragment weakens the screening of the C-3 and C-4 atoms of a Δ^5-spirostene aglycone to a greater extent than the $(OAc)_3$-α-Rhap-(1→4) fragment.

3. The C-1''' and C-5''' atoms of a $(OAc)_3$-α-L-Rhap-(1→2) unit are considerably more screened than the C-1'' and C-5'' atoms of a $(OAc)_3$-α-L-Rhap-(1→4) unit, and the α glycosidation shifts for the attached monosaccharides are opposite in sign.

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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.

VII. STRUCTURES OF CYCLOSIEVERSIOSIDES A AND C

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Two new glycosides, cyclosieversiosides A and C, have been isolated from the roots of *Astragalus sieversianus* Pall. Cyclosieversioside A is cyclosieversigenin 3-O-(2',3'-di-O-acetyl-β-D-xylopyranoside) 6-O-β-D-xylopyranoside. Cyclosieversioside C is cyclosieversigenin 3-O-(2'-O-acetyl-β-D-xylopyranoside) 6-O-β-D-xylopyranoside.

We have previously reported the structures of two glycosides of the cycloartane series, cyclosieversiosides E [1] and F [2], isolated from *Astragalus sieversianus* Pall. The present paper is devoted to a determination of the structures of two new glycosides — cyclosieversiosides A (III) and C (I) (substances A and C, respectively), isolated from the roots of the same plant [1].

Absorption bands in the IR spectrum of (I) at 1750 and 1260 cm^{-1} and also a three-proton signal at 1.89 ppm permitted the assumption of the presence of an acetate group in the molecule of the compound under investigation.

Sapinification of the glycoside (I) with a 0.25% methanolic solution of potassium hydroxide gave cyclosieversioside E — cyclosieversigenin 3,6-di-O-β-D-xylopyranoside (II) [1].

The position of the acetyl residue was determined from the feature of the ^1H and ^{13}C NMR spectra of compounds (I), (II), and (IV).

In the ^{13}C NMR spectrum of cyclosieversigenin 3-O-β-D-xylopyranoside (IV), which has been described previously [2], the signal of the C-1' atom appears at 107.3 ppm. In the spectrum of cyclosieversioside E (II), the anomeric carbon atoms resonate at 107.3 and 105.3 ppm. It follows from a comparison of these facts that these values of the chemical shifts relate, respectively, to the C-1' and C-1'' atoms of D-xylose residues located at C-3 and C-6 in the cyclosieversioside E (II) molecule.

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