SUMMARY

A new triglycoside of the cycloartane series has been isolated from the roots of *Astragalus sieversianus* Pall.; it is cyclosiversigenin 6-O-β-D-glucopyranoside 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-xylopyranoside].

LITERATURE CITED

1. A. N. Svechnikova, P. U. Umarov, M. B. Gorovits, N. A. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 312 (1983).
2. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 204 (1982).
3. T. T. Gorovits, Khim. Prir. Soedin., 263 (1970).
4. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 208 (1982).
5. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, K. L. Seitanidi, Ya. V. Rashkes, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 67 (1981).
6. K. Tori, S. Seo, Y. Yashimura, M. Nakamura, Y. Tomita, and H. Ishii, Tetrahedron Lett., 4167 (1967).
7. L. I. Strigina and V. V. Isakov, Khim. Prir. Soedin., 847 (1980).
8. W. Klyne, Biochem. J., 47, XLI (1950).

---

^{13}C NMR SPECTRA OF STEROID GLYCOSIDES.

III. ACETATES OF PENNOGENIN TRIOSIDES

L. I. Strigina and V. V. Isakov

UDC 547.917+547.918+543.422.25

The ^{13}C NMR spectra of two pennogenin trioside acetates have been measured and an assignment has been made of the signals of the C atoms. The mutual influence of the aglycone and of the acetylated carbohydrate chains, and also of the acetylated monosaccharides composing the carbohydrate chains, have been determined.

One of the promising methodological approaches to determining the structures of natural spirostanol glycosides is ^{13}C NMR spectroscopy. Investigations in this direction have been successfully developed in recent years [1-7]. However, the great complexity of the ^{1}H NMR spectra of the free glycosides prevents the unambiguous assignment of the signals in the ^{13}C NMR spectra by using the method of selective decoupling from protons. The spectroscopy of the acetates of glycosides has a number of advantages due to the lesser complexity of the ^{1}H NMR spectra and the good solubility of the acetates of the glycosides in a large number of nonpolar solvents.

We have studied the ^{13}C NMR ($CDCl_3$) spectra of two acetates of spirostanol glycosides — polygonatosides C^1 (I) and C^2 (II) [8]. We report the assignment of the resonance signals of the C atoms in the spectra.

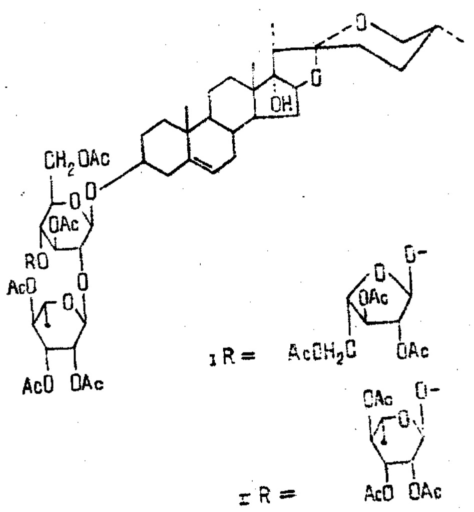
The assignment of the signals of the C atoms in the ^{13}C NMR spectra of (I) and (II) was carried out on the basis of results for pennogenin [9] and those given in the literature for the corresponding methyl glycosides [10].

To illustrate the mutual influence of the aglycone and the component carbohydrate chains, we calculated the glycosylating shifts $\Delta\delta = \delta_C$ of the glycoside acetate — δ_C of the aglycone (for the aglycone), and $\Delta\delta = \delta_C$ of the glycoside acetate — δ_C of the acetate of the methyl glycoside (for the acetylated monosaccharides) [4]. The glycosylation shifts for the $(OAc)_3$-α-L-Ara*f* residues of (I) are not given because of the absence from the literature of informa-

---

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Pirodnykh Soedinenii, No. 4, pp. 463-465, July-August, 1983. Original article submitted June 14, 1982.

0009-3130/83/1904-0434$07.50



tion on the ^{13}C NMR spectrum of methyl $(OAc)_3$-α-L-arabinofuranoside. The chemical shifts of the signals of the aglycone (ring A) and carbohydrate moieties of (I) and (II) and the glycosylation shifts are given in Table 1.

The signals of the C atoms of the aglycone moieties of (I) and (II), with the exception of the signals of ring A, are close to those of pennogenin [9]. The values and directions of the glycosylation shifts for the C-3 (α), C-2 (β), and C-4 (β) atoms of the aglycone of (I) and (II) are close to those of the free glycosides of steroid 3(β)-hydroxy alcohols of the spirostan series [4].

In the ^{13}C NMR ($CDCl_3$) spectrum of (I), the assignment of the signals of the $(OAc)_3$-α-L-Rhap unit (C") and of the $(OAc)_3$-α-L-Araf unit (C"') was made by selective decoupling from protons. ^1H NMR ($CDCl_3$) spectrum of (I) (δ, ppm): HC-1" 4.99, HC-2" 5.01, HC-3" 5.25, HC-4" 5.06, HC-5" 4.39, HC-6 1.19; HC-1"' 4.97, HC-2"' 4.94, HC-3"' 4.94, HC-4"' 4.20 HC-5"' in the 4-4.5 region. In the ^{13}C NMR ($CDCl_3$) spectrum of (II) the signals of the two $(OAc)_3$-α-L-Rhap units attached by 1 → 2-(C") and 1 → 4(C"") bonds form separate regions not overlapping with that of the $(OAc)_2$-β-D-Glcp unit, and they differ greatly with respect to the degree of screening of their C-1, C-4, and C-5 atoms.

For the $(OAc)_3$-α-L-Rhap-(1 → 2) unit, C-1" and C-5" are more screened, and C-4" is less screened than the corresponding C atoms (C"') of the $(OAc)_3$-α-L-Rhap-(1 → 4) unit when they are present together in a branched carbohydrate chain. Furthermore, the α glycosylation shifts for the attached acetylated rhamnosyl units are opposite in sign.

The assignment of the signals of the C atoms of the $(OAc)_2$-β-D-Glcp unit in (I) and (II) is based on the results for Me-$(OAc)_4$-β-D-Glcp [10] and for (I) it was confirmed by selective decoupling from protons. ^1H NMR ($CDCl_3$) spectrum of (I) (δ, ppm): HC-1' 4.55, HC-2' 3.61, HC-3' 5.28, HC-4' 3.67, HC-5' 3.62, H_2C-6' 4.25 and 4.4.

It follows from the spectrum of (II) that the addition of two $(OAc)_3$-α-L-Rhap residues to C-2' and C-4' gives a downfield shift of the signals of all the C atoms of the glycosyl unit apart from that of C-1'. It is obvious from a comparison of the spectra of (I) and (II) that the replacement of a $(OAc)_3$-α-L-Rhap unit at C-4' by a $(OAc)_3$-α-L-Araf unit affects the glycosylation shifts observed for the C atoms of the glycosyl unit. It is shown in a small increase in the degree of screening of the C-4' (α) and the neighboring C-3' (β) atoms and a decrease in the degree of screening of the C-5' (β) and C-6' (γ) atoms.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra of (I) were recorded on a WM-250 spectrometer at working frequencies of 250 and 60.9 MHz, respectively. The accuracy of the measurement of the chemical shifts was ±0.02 ppm (^{13}C) and 1 Hz (^1H). The ^{13}C NMR spectrum of (II) was recorded on a Bruker HX-90 spectrometer at a working frequency of 22.63 MHz. The accuracy of the measurements of the chemical shifts was ±0.05 ppm. Solutions of (I) and (II) in $CDCl_3$ with concentrations of ~5% were used at 30°C, with TMS as internal standard. The acetates (I) and (II) were obtained from the corresponding glycosides as described previously [8].

TABLE 1. ^{13}C Chemical Shifts δ (ppm) and Glycosylation Shifts Δδ (ppm) of the C Atoms of Aglycone (ring A) and of the Carbohydrate Moieties of Polygonatosides C^1 (I) and C^2 (II)

C atom	I		II	
	δ	Δδ	δ	Δδ
1	37,2	—0,1	37,2	—0,1
2	29,6	—2,0	29,6	—2,0
3	79,3	+7,7	79,15	+7,55
4	38,4	—3,9	38,3	—4,0
5	140,3	—0,6	140,1	—0,8
6	122,0	+0,7	122,0	+0,7
1′	99,6	—1,9	99,5	—2,0
2′	76,3	+5,0	76,4	+5,1
3′	74,9	+2,0	75,3	+2,4
4′	77,5	+9,0	77,7	+9,2
5′	72,8	+1,0	72,3	+0,5
6′	62,5	+0,5	62,3	+0,3
1″	97,5	—1,0	97,3	—1,2
2″	70,4	+0,6	70,2*	+0,4
3″	68,7	—0,5	68,6	—0,6
4″	71,5	+0,5	71,3*	+0,3
5″	66,4	+0,1	66,4	+0,1
6″	17,3	—0,1	17,3	—0,1
1‴and1⁗	107,6		99,5	+0,1
2‴and2⁗	81,5		70,1*	+0,3
3‴and3⁗	76,6		68,6	—0,6
4‴and4⁗	81,6		70,6*	—0,4
5‴and5⁗	63,3		67,9	+1,6
6⁗	—		17,1	—0,3
$\underline{C}H_3\cdot CO$	20,7; 20,8; 21,2		20,8; 21,3	
$CH_3\cdot \underline{C}O$	169,6; 169,9; 170,5		169,6; 169,9; 170,5	

*The assignments may be interchanged within the vertical column.

SUMMARY

1. The mutual influence of the aglycones and the acetylated carbohydrate chains, and also of the acetylated monosaccharides, composing the branched carbohydrate chains of two pennogenin trioside acetates has been determined.

2. The chemical shifts of the signals of the C atoms of the $(OAc)_3$-α-L-Ara*f*(1 →) unit have been determined.

LITERATURE CITED

1. R. U. Lemieux, R. M. Ratcliffe, B. Arreguin, A. Romo de Vivar, and M. J. Castillo, Carbohydr. Res., 55, 113 (1977).
2. R. J. Weston, H. E. Gottlieb, and E. W. Haggaman, Aust. J. Chem., 30, 917 (1977).
3. L. O. Strigina, E. V. Kol'chuk, and V. V. Isakov, Khim. Prir. Soedin., 711 (1977).
4. S. Seo, J. Tomita, K. Tori, J. Joshimura, J. Am. Chem. Soc., 100, 3331 (1978).
5. T. Konishi and J. Shoji, Chem. Pharm. Bull., 27, 3086 (1979).
6. L. I. Strigina and V. V. Isakov, Khim. Prir. Soedin., 847, 848 (1980).
7. S. B. Mahato, N. P. Sahu, and A. N. Ganguly, Indian J. Chem., 19B, 817 (1980).
8. L. I. Strigina, E. V. Kol'chuk, and E. I. Pilipenko, Khim. Prir. Soedin., 121 (1977).
9. L. I. Strigina, E. V. Kol'chuk, A. I. Kalinovskii, and V. V. Isakov, Khim. Prir. Soedin., 580 (1977).
10. A. I. Kalinovskii and E. V. Evtushenko, Khim. Prir. Soedin., 6 (1979).