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.

LITERATURE CITED

1. R. U. Lemieux, R. M. Ratcliffe, B. Arreguin, A. Rome de Vivar, and M. J. Castillo, Carbohydr. Res., 55, 113 (1977).
2. R. J. Weston, H. E. Gottlieb, and E. W. Hagaman, Aust. J. Chem., 30, 917 (1977).
3. T. Konishi and J. Shoji, Chem. Pharm. Bull., 27, 3086 (1979).
4. L. I. Stringina and V. V. Isakov, Khim. Prir. Soedin., 847 (1980).
5. L. L. Stringina and V. V. Isakov, Khim. Prir. Soedin., 848 (1980).
6. V. A. Paseshnichenko, A. R. Guseva, L. I. Strigina, and V. V. Isakov, Dokl. Akad. Nauk SSSR, 256, 742 (1981).
7. L. I. Strigina, E. V. Kol'chuk, and V. V. Isakov, Khim. Prir. Soedin., 711 (1977).
8. S. Seo, Y. Tomita, K. Tori, and Y. Yoshimura, J. Am. Chem. Soc., 100, 3331 (1978).
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).
11. A. I. Kalinovskii and N. S. Chetyrina, Khim. Prir. Soedin., 359 (1980).

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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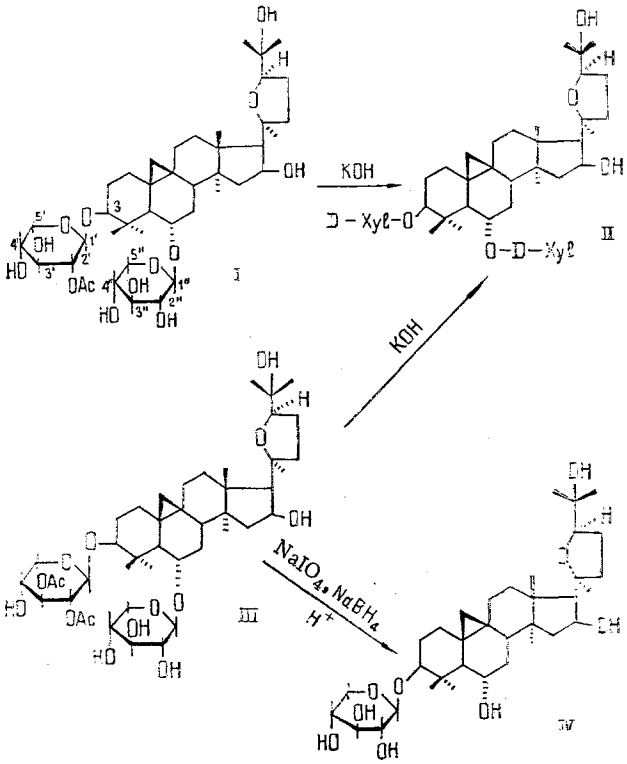

In the ^{13}C NMR spectrum of cyclosieversioside C (I), the signals of the anomeric carbon atoms are located at 104.5 and 105.3 ppm. A comparison of the values of the chemical shifts of these carbon atoms in compounds (I) and (II) shows that the signal of the C-1' atom has undergone a diamagnetic shift by 2.8 ppm [$\Delta\delta = \delta(C\text{-}1')_{II}$ 107.3 − δ $(C\text{-}1')_{I}$ 104.5 = 2.8 ppm]. This proves that the acyl residue is present in the xylose molecule attached to C-3 of the aglycone. The same value of the upfield shift of the C-1' carbon atom by 2.8 ppm shows the location of the acetyl group on the neighboring carbon atom (C-2') [3]. This conclusion agrees well with the results of the study of the multifrequency PMR spectrum of cyclosieversioside C (I).

In the PMR spectrum of compound (I) there is a one-proton triplet (Σ^3J = 14 Hz) at 5.32 ppm belonging to a proton located geminally to an acetyl group. Doublet signals of anomeric protons with ^3J = 7.5 and 6.1 Hz, respectively, appear in the same spectrum at 4.55 and 4.67 ppm. On the superposition of an additional radiofrequency field with ν = 455 Hz (H-1'), the triplet at 5.32 ppm was converted into a doublet with ^3J = 6.5 Hz. Simultaneous irradiation at the frequencies ν = 455 and 394 Hz (H-3') led to the transformation of the signal under consideration into a singlet. This clearly shows a chain of interacting protons: C_1'H(O)—C_2'H(OAc)—C_3'H(OH).

The experimental results presented permit the conclusion that cyclosieversioside C (I) has the structure of cyclosieversigenin 3-O-(2'-O-acetyl-β-D-xylopyranoside) 6-O-β-D-xylopyranoside.

Cyclosieversioside A (III) also has an ester function in its composition. Absorption in the IR spectrum of glycoside (III) at 1757, 1725, and 1235-1265 cm^{-1}, and the presence in the PMR spectrum of two three-proton singlets at 1.87 and 1.82 ppm, gave grounds for considering that this glycoside contains two acetate groups.

The saponification of the diacetylglycoside (III) with 0.25% methanolic potassium hydroxide showed that its molecule was also based on cyclosieversioside E (II).

In the ^{13}C NMR spectrum of cyclosieversioside A (III), the anomeric carbon atoms resonate at 103.8 and 105.3 ppm. In a comparison of the values of the chemical shifts of the anomeric carbon atoms of cyclosieversioside E (II) [δ (C-1') = 107.3; δ (C-1") = 105.3 ppm] and its diacetyl derivative (III), it is not difficult to observe that the C-1" signal in the spectrum of (III) has retained its position (105.3 ppm) while the signal from the C-1' atom (103.8 ppm) has undergone a diamagnetic shift by 3.5 ppm. This permitted us to conclude that one of the acetyl groups in compound (III) is undoubtedly present at C-2'. The position of

the other acetyl residue was established by an analysis of the multifrequency PMR spectrum of cyclosieversioside A (III).

In the PMR spectrum of the diacylglycoside (III), triplet signals from protons geminal to acetyl groups are found at 5.18 and 5.41 ppm, with Σ^3J = 14.7 and 18.8 Hz, respectively. Doublets from the anomeric protons appear at 4.58 and 4.66 ppm. The superposition of an additional radiofrequency field with ν = 458 Hz (H-1') converted the triplet at 5.18 ppm (H-2') into a doublet with ^3J = 8.1 Hz. It changed further into a singlet on the simultaneous action of the frequencies ν = 458 and 541 Hz. On the other hand, the triplet at 5.41 ppm was converted into a doublet with ^3J = 9.7 Hz on saturation of the transitions of nuclei resonating at 3.90 ppm (H-4').

The facts presented indicate that the signal at 5.41 ppm belongs to the proton at C-3' and shows that the second acetyl group is located on the same carbon atom.

Consequently, in cyclosieversioside A (III), acetic acid esterifies the hydroxy groups at C-2' and C-3' of the D-xylose residue attached through the hydroxy group at C-3.

What has been said above gives us grounds for concluding that cyclosieversioside A (III) has the structure of cyclosieversigenin 3-O-(2',3'-di-O-acetyl-β-D-xylopyranoside) 6-O-β-D-xylopyranoside.

As was to be expected, the Smith degradation [5] of cyclosieversioside A led to the formation of the monoside (IV) [2].

EXPERIMENTAL

For general observations and methods, see [1, 4]. PMR spectra were taken in C_5D_5N on a JNM-4H-100/100 MHz instrument (δ, 0 — HMDS), and ^{13}C NMR spectra on a Varian CFT-20 instrument in C_5D_5N (0 — TMS).

Cyclosieversioside C (substance C, I) [1]. $C_{42}H_{68}O_{14}$, mp 253-255°C (from methanol), $[\alpha]_D^{20}$ +30.1 ± 2° (c 0.97; methanol). ν_{max}^{KBr}, cm^{-1}: 3360-3500 (OH), 1750, 1260 (ester group), PMR spectrum (δ, ppm): 0.44 (1 H at C-19), 0.96 s (CH_3), 1.06 s (CH_3), 1.16 s ($CH_3 \times 2$), 1.25 s (CH_3), 1.41 s (CH_3), 1.52 s (CH_3), 1.89 s (CH_3CO).

Alkaline Hydrolysis of Cyclosieversioside C (I). A solution of 50 mg of cyclosieversioside C in 15 ml of methanol was treated with 15 ml of a 0.5% solution of KOH in the same solvent. The reaction mixture was left at room temperature for 2 days. Then 100 ml of water was added, the methanol was distilled off, and the reaction products were extracted with n-butanol. The butanolic extract was washed with water and evaporated to dryness. As a result, after recrystallization from methanol, 31 mg of cyclosieversioside E (II) was obtained with mp 257-259°C, $[\alpha]^{20}$ +30.1 ± 2°(c 0.68; methanol) shown to be identical with an authentic sample [1] also by the feature of its IR spectrum and its R_f value in TLC.

Cyclosieversioside A (substance A, III) [1]. $C_{44}H_{70}O_{15}$, mp 230-232°C (from methanol), $[\alpha]_D^{20}$ +23.8 ± 2° (c 0.84; methanol). ν_{max}^{KBr}, cm^{-1}: 3370-3430 (OH), 1725, 1757, 1235-1265 cm^{-1} (ester groups). PMR spectrum (δ, ppm) 0.44 (1 H at C-19), 0.95 s (CH_3), 1.05 s (CH_3), 1.16 s ($CH_3 \times 2$), 1.25 s (CH_3), 1.42 s (CH_3), 1.50 s (CH_3), 1.82 s (CH_3CO), 1.87 s (CH_3CO).

Alkaline Hydrolysis of Cyclosieversioside A (III). A solution of 100 mg of cyclosieversioside A (III) in 30 ml of methanol was treated with 30 ml of a 0.5% solution of KOH in the same solvent. The reaction mixture was left at room temperature for 2 days. Then 200 ml of water was added, the methanol was distilled off, and the reaction products were extracted with n-butanol. Washing the butanolic extract with water and evaporating to dryness gave 40 mg of the glycoside (II) with mp 256-258°C (from methanol), $[\alpha]_D^{20}$ +29.0 ± 2° (c 0.65; methanol), identical with an authentic sample of cyclosieversioside E (II) [1].

Smith Degradation of Cyclosieversioside A (III) [5]. A solution of 300 mg of cyclosieversioside A in 300 ml of aqueous methanol (1:1) was treated with 600 mg of sodium periodate and the mixture was stirred at room temperature for 20 h. The unconsumed oxidant was decomposed with ethylene glycol. Then the methanol was evaporated off, the residue was treated with 100 ml of water, and the reaction products were extracted with chloroform. The chloroform was distilled off to dryness, 200 ml of aqueous methanol (1:1) and 610 mg of sodium tetrahydroborate were added to the residue, and the mixture was heated at 80°C for 7 h. After cooling, the reaction mixture was acidified to pH 2.0 and was left at room temperature for 18 h. Then the reaction products were extracted with chloroform, the solvent was evap-

porated off, and the residue was recrystallized from methanol. This gave 180 mg of cyclosieversigenin 3-O-β-D-xylopyranoside (IV) with mp 259-261°C, $[\alpha]_D^{20}$ +42.0 ± 2° (c 0.60; methanol), identical with an authentic sample [2] according to R_f value and IR spectral characteristics.

SUMMARY

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

LITERATURE CITED

1. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 204 (1982).
2. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 208 (1982).
3. K. Yamasaki, R. Kasai, Y. Masaki, M. Okihara, O. Tanaka, H. Oshio, S. Takagi, M. Yamaki, K. Masuda, G. Nanaka, M. Tsuboi, and I. Nishioka, Tetrahedron Lett., 1231 (1971).
4. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, K. A. Seitanidi, Ya. V. Rashkes, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 67 (1981).
5. M. Abdel-Akher, J. K. Hamilton, R. Montgomery, and F. Smith, J. Am. Chem. Soc., 74, 4970 (1952).

ALKALOIDS OF *Nitraria komarovii*.

V. STRUCTURE AND SYNTHESIS OF KOMAROVICINE

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The new alkaloid komarovicine has been isolated from the epigeal part of the plant *Nitraria komarovii* Iljin et Lava. Its structure has been established on the basis of spectral and experimental results and its synthesis has been performed. A transition has been made to the alkaloids komarovine and komarovidine isolated previously.

Continuing an investigation of the alkaloids of *Nitraria komarovii* Iljin et Lava [1], from the combined fractions with pH 5, 6, and 7 after the separation of komarovine [2] and komarovidine [3], by chromatography on a column we have isolated a base with mp 209-210°C (CH_2Cl_2) having the composition $C_{20}H_{17}N_3$, $[\alpha]_D \pm 0°$, which we have called komarovicine (I).

In the mass spectrum of the alkaloid there are the peaks of the ions with m/z 299 (M^+, 100%), 283 (20), 282 (52), 281 (44), 271 (30), 270 (28), 269 (54), 149.5 M^{++}.

In the UV spectrum there are absorption maxima characteristic for indole and quinoline: $\lambda_{max}^{ethanol}$ 220, 275-286, 294, 318 (lg ε 4.75, 4.14, 4.13, 3.68), $\lambda_{max}^{ethanol+H^+}$ 225, 272, 283, 316. The IR spectrum contains the absorption bands due to an indole nucleus (1460, 1505, 1580, 1620, cm^{-1}) and to methylene and methine groups (2860, 2940 cm^{-1}).

The PMR spectrum contains, in addition to a complex group of signals in the aromatic region, two two-proton multiplets at 2.81 and 2.99 ppm (Ar—CH_2—CH_2—N<H) and two one-

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