Chemistry of Natural Compounds, Vol. 31, No. 6, 1995

TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.
LII. ASKENDOSIDE F FROM *Astragalus taschkendicus*

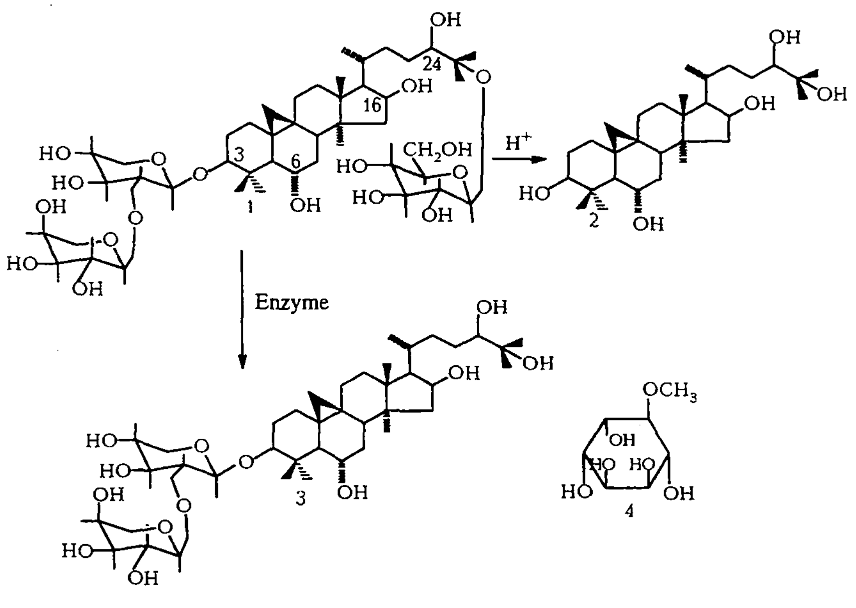
M. I. Isaev

UDC 547.918:547.926

The roots of Astragalus taschkendicus *Bunge (Leguminosae) have yielded the new cycloartane glycoside askendoside F, which is 24R-cycloartan-3β,6α,16β,24,25-pentaol 3-O-[O-α-*L*-arabinopyranosyl-(1→2)-β-*D*-xylopyranoside] 25-O-*D*-glucopyranoside, and *D*-3-O-methyl-*chiro*-inositol.*

Continuing a study of the cycloartanes of *Astragalus taschkendicus* Bunge [1], from the polar fraction of a methanolic extract of the roots of this plant we have isolated two new glycosides, which we have called askendosides E and F, and compound (4), identified as *D*-3-O-methyl-*chiro*-inositol [2, 3]. In the present paper we give proof of the structure of askendoside F (1).

The presence in the PMR spectrum of glycoside (1) of two one-proton doublets of an *AB* system at 0.28 and 0.58 ppm and also of the signals of seven methyl groups in the high-field permitted us to assign the new glycoside to methylsteroids of the cycloartane series. It was shown by the GLC method [6] that askendoside F contains *D*-glucose, *D*-xylose, and *L*-arabinose residues in a ratio of 1:1:1. In agreement with this, in the ^1H and ^{13}C NMR spectra of the new glycoside (1) we observed the signals of three anomeric protons, at 4.92, 5.18, and 5.21 ppm, and of the carbon atoms of three monosaccharide residues (Table 1).



Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (3712) 89 14 75. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 820-823, November-December, 1995. Original article submitted May 15, 1995.

0009-3130/95/3106-0690$12.50

TABLE 1. Chemical Shifts of the Carbon Atoms of Compounds (**1-3**) (δ, ppm, 0−TMS, C_5D_5N)

C atom	Compound		
	1	**2**	**3**
1	32.51	32.77	32.45
2	29.22[a]	31.41	29.13
3	88.52	78.32	88.44
4	42.75	42.40	42.67
5	54.12	53.95	53.98
6	67.94	68.27	67.91
7	38.40	38.59	38.33
8	46.94	47.22	46.92
9	21.34	21.26	21.25
10	30.35	30.38	30.29
11	26.31	26.35	26.25
12	33.18	33.17	33.11
13	45.68	45.68	45.61
14	46.84	46.91	46.78
15	48.62	48.75	48.55
16	71.80	71.72	71.67
17	57.32	57.24	57.20
18	18.77	18.79	18.71
19	29.93	29.36	29.95
20	31.53	31.59	31.51
21	18.93	19.08	18.92
22	29.22[a]	29.56	29.33
23	34.94	34.82	34.78
24	78.94	80.53	80.42
25	80.90	72.68	72.68
26	21.54*	25.90*	25.81*
27	24.22*	26.13*	26.01*
28	20.17	20.28	20.14
29	28.63	29.37	28.54
30	16.24	16.13	16.18
	β-D-Xyl*p* residue		
1	105.59		105.53
2	83.55		83.47
3	77.58		77.48
4	70.97		70.25
5	66.57		66.48
	α-L-Ara*p* residue		
1	106.61		106.52
2	73.63		73.51
3	74.28		74.16
4	69.11		69.02
5	66.98		66.90
	β-D-Glc*p* residue		
1	98.69		
2	75.34		
3	78.73		
4	71.71		
5	78.19		
6	62.80		

Note: Signals labeled with the same letters are superposed on one another, and the assignment of those with asterisks is ambiguous.

The acid hydrolysis of glycoside (**1**) gave the genin (**2**), which was identified as cycloasgenin C.

A comparative analysis of the ^{13}C NMR spectra of cycloasgenin C and askendoside F showed that the C-3 and C-25 atoms in the latter had suffered glycosylation effects and resonated at 88.52 and 80.90 ppm, respectively. In the spectrum of the genin (**2**) the signals of the same atoms were observed at 78.32 and 72.68 ppm. Consequently, the new glycoside (**1**) was a bisdesmoside, one of the carbohydrate chains of which was located at C-3 and the other at the tertiary C-25 atom.

The enzymatic hydrolysis of askendoside F by the gastric juice of the grape snail *Helix pomatia* gave askendoside C (**3**) [7]. This meant that glycoside (**1**) contained an *α-L*-arabinopyranosyl-(1→2)-*β-D*-xylopyranoside disaccharide residue attached to the genin at C-3, and a *D*-glucose residue at C-25. The signal of the anomeric carbon atom of the *D*-glucose residue, which was observed at 98.69 ppm, confirmed the conclusion that a hexose was located at a tertiary hydroxy group. In the PMR spectrum of askendoside F, the anomeric proton of the *D*-glucose residue resonated at 5.18 ppm in the form of a doublet with the SSCC J = 8 Hz. Consequently, the *D*-glucose residue had the pyranose form, the $^4C_1$-conformation, and the *β*-configuration. A calculation of molecular rotation differences agreed with this conclusion.

Thus, askendoside F is 24R-cycloartane-3β,6α,16β,24,25-pentaol 3-O-[O-α-*L*-arabinopyranosyl-(1→2)-β-*D*-xylopyranoside] 25-O-*D*-glucopyranoside.

EXPERIMENTAL

General Observations. The following solvent systems were used: 1) chloroform–methanol–water (70:23:4); 2) ethyl acetate–methanol (3:1); 3) chloroform–methanol (15:1).

For the TLC, CC, and GLC conditions, see [6].

^{1}H and ^{13}C NMR spectra were taken on a Bruker AM 400 spectrometer having a working frequency for ^{1}H nuclei of 400.134 MHz and for ^{13}C nuclei of 100.614 MHz, in deuteropyridine (δ, ppm, 0–TMS). ^{13}C NMR spectra were taken with complete and with partial suppression of interactions with protons, and also under J-modulation conditions.

For the isolation and separation of the triterpenoids of *Astragalus taschkendicus* Bunge, see [1]. After the isolation of askendoside D [8], elution of the column with system 1 led to the appearance of chromatographically homogeneous fractions containing askendosides E and F and *D*-3-O-methyl-*chiro*-inositol. The askendosides E and F were each chromatographed repeatedly on a column of silica gel in systems 1 and 2. This gave 925 mg of askendoside E (0.0174% yield on the air-dry raw material) and 100 mg of askendoside F (0.0019%).

The fractions containing *D*-3-O-methyl-chiro-inositol were recrystallized from methanol, giving 350 mg of compound (4) (0.0066%).

Askendoside F (1), $C_{46}H_{78}O_{18}$, amorphous, $[\alpha]_D^{24}$ 0 ± 3° (*c* 0.7; MeOH). IR spectrum (KBr, ν, cm^{-1}): 3392 (OH). PMR spectrum (400 MHz, C_5D_5N, δ, ppm, 0–TMS, J, Hz): 0.28 and 0.58 (2H-19, d, $^2J = 4$), 1.01 (CH_3, s), 1.07 (CH_3-21, d, $^3J = 6.5$), 1.38; 1.42; 1.47; 1.49; 1.95 (5 × CH_3, s), 4.92 (H-1 *D*-xylose, d, $^3J = 7$), 5.18 (H-1 *D*-glucose, d, $^3J = 8$), 5.21 (H-1 *L*-arabinose, d, $^3J = 6$). For the ^{13}C NMR spectrum, see Table 1.

It was shown by the GLC method [6] that askendoside F contained *D*-glucose, *D*-xylose, and *L*-arabinose residues in a ratio of 1.00:1.20:0.94.

***D*-3-O-Methyl-*chiro*-inositol (4)**, $C_7H_{14}O_6$, mp 185-186°C (from MeOH), $[\alpha]_D^{25}$ + 65 ± 2° (*c* 0.5; H_2O) [2, 3]. PMR spectrum (400 MHz, C_5D_5N, δ, ppm, 0–TMS, J, Hz): 3.91 (CH_3O, s), 4.12 (1H, t, $^3J = 9$), 4.60 (1H, t, $^3J = 9$), 4.68-4.77 (4H, m). ^{13}C NMR spectrum (100 MHz, C_5D_5N, δ, ppm, 0–TMS): 85.79 (d), 74.66 (d), 74.16 (d), 73.71 (d), 73.07 (d), 72.26 (d), 60.72 (q).

Cycloasgenin C from (1). Glycoside (1) (44 mg) was hydrolyzed with 5 ml of 1% aqueous sulfuric acid at 40°C for 8 h. Then the reaction mixture was diluted with water and was treated with *n*-butyl alcohol. After evaporation of the solvents the butanolic fraction was chromatographed on a column with elution by system 3. This led to the isolation of 11 mg of cycloasgenin C (2), mp 244-246°C [from $(CH_3)_2CO$], $[\alpha]_D^{25}$ + 34 ± 2° (*c* 0.8; methanol). PMR spectrum (400 MHz, C_5D_5N, δ, ppm. 0–TMS, J, Hz): 0.33 and 1.47; 1.49; 1.87 (5 × CH_3, s), 3.66 (H-3, dd, $^3J_1 = 12$, $^3J_2 = 5$), 3.77 (H-24, dd, $^3J_1 = 10$, $^3J_2 = 2$), 3.80 (H-6, td, $^3J_1 = {}^3J_2 = 10$, $^3J_3 = 3$), 4.70 (H-16, td, $^3J_1 = {}^3J_2 = 8$, $^3J_3 = 5$). For the ^{13}C NMR spectrum, see Table 1.

Askenoside C (3) from (1). Glycoside (1) (48 mg in 10 ml of water) was treated with 30 mg of the freeze-dried gastric juice of the grape snail *Helix pomatia* and 1 drop of benzene. The mixture was left at room temperature for 30 days, after which the solution was diluted with water and was treated with *n*-butyl alcohol. The residue after evaporation of the solvents was chromatographed on a column and was eluted by system 1, with the isolation of 15 mg of askendoside C (3), mp 197-198°C (from MeOH), $[\alpha]_D^{25}$ + 27 ± 2° (*c* 1.0; MeOH). PMR spectrum (400 MHz, C_5D_5N, δ, ppm, 0–TMS, J, Hz): 0.27 and 0.54 (2H-19, d, $^2J = 4$), 0.97 (CH_3, s), 1.08 (CH_3-21, d, J = 6), 1.33; 1.36; 1.41; 1.44; 1.91 (5 × CH_3, s), 4.68 (H-16, m), 4.87 (H-1 of *D*-xylose, d, $^3J = 6$), 5.16 (H-1 of *L*-arabinose, d, $^3J = 6$). For the ^{13}C NMR spectrum, see Table 1.

REFERENCES

1. M. I. Isaev, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 458 (1982).
2. S. J. Angyal and L. Odier, Carbohydr. Res. **123**, 23 (1983).
3. N. A. El-Sebakhy, F. M. Harraz, R. M. Abdallah, A. M. Assad, F. Orsini, F. Pelizzoni, G. Sello, and L. Verotta, Phytochemistry, **29**, 3271 (1990).

4. M. I. Isaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 431 (1985).
5. M. I. Isaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 156 (1989).
6. M. A. Agzamova, M. I. Isaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 719 (1986).
7. M. I. Isaev, M. B. Gorovits, T. T. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 173 (1983).
8. M. I. Isaev, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 180 (1983).