*Chemistry of Natural Compounds, Vol. 44, No. 3, 2008*

# CYCLOASCAULOSIDE B FROM *Astragalus caucasicus*

**M. D. Alaniya,[1*] N. Sh. Kavtaradze,[1]**
**R. Faure,[2] and L. Debrauwer[2]**

UDC 547.918:547.926

*The structure of a new cycloartane glycoside isolated from leaves of* Astragalus caucasicus *Pall. (Leguminosae) was elucidated using chemical transformations and spectral data. Cycloascauloside B is 20*R*,25-epoxy-24*S*-cycloartan-3β,6α,16β,24-tetraol 3-*O*-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside.*

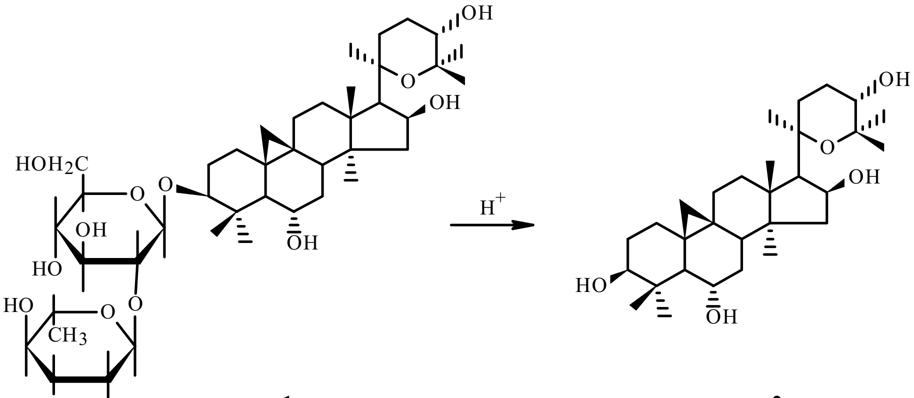
**Key words:** triterpenes, *Astragalus*, PMR and $^{13}$C NMR spectroscopy, DEPT, cyclocephalogenin, cycloascaulosides A and C.

In continuation of chemical research on 9,19-cycloartane triterpenoids, we elucidated the structure of a new glycoside isolated from leaves of *Astragalus caucasicus* Pall. (L., Leguminosae) that we called cycloascauloside B (**1**) [1, 2].

The IR, PMR, and $^{13}$C NMR spectra indicated that the studied glycoside was a cycloartane derivative [3, 4].

The PMR spectrum of **1** showed resonances at 0.20 and 0.52 ppm for protons of an isolated cyclopropane methylene. Compound **1** was hydrolyzed by acid in order to obtain **2**. TLC of the aqueous part of the acid hydrolysate detected D-glucose and L-rhamnose. The $^{13}$C NMR spectrum of the glycoside contained resonances for two carbohydrates. Also, the PMR spectrum of the glycoside exhibited resonances for all 12 protons of two monosaccharides. Therefore, cycloascauloside B was a bioside containing D-glucose and L-rhamnose in a 1:1 ratio.

Anomeric protons of the monosaccharides of **1** resonated in the PMR spectrum at 4.92 (8 Hz) and 5.70 ppm(1.3 Hz). The SSCC were consistent with the *β*-configuration of D-glucose and the pyranose form of the monosaccharides [5, 6].



**1** **2**

---

1) I. G. Kutateladze Institute of Pharmaceutical Chemistry, Academy of Sciences of Georgia, Tbilisi, 0159, ul. Sarajishvili, 36, Republic of Georgia, fax (99532) 25 00 26, e-mail: merialania@yahoo.com; 2) UMR 6009 Universite d'Aix-Marseille III, Avenue Escadrille Normandie Neimen 13397, Marseille, cedex 20, France. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 257-258, May-June, 2008. Original article submitted February 18, 2008.

0009-3130/08/4403-0324

TABLE 1. Chemical Shifts of C and H Atoms in Cycloascauloside B (**1**) and Cyclocephalogenin (**2**) (δ, ppm, $C_5D_5N$, TMS)

| C atom | **1** | | | **2** |
|---|---|---|---|---|
| | $\delta_C$ | DEPT | $\delta_H$ | $\delta_C$ |
| 1 | 32.64 | $CH_2$ | 1.53; 1.23 | 32.0 |
| 2 | 30.50 | $CH_2$ | 2.29 m, 1.95 | 30.4 |
| 3 | 88.80 | CH | 2.60 dd (11.7; 4.4) | 78.7 |
| 4 | 42.62 | C | - | 42.0 |
| 5 | 54.26 | CH | 1.88 d (8.6) | 53.8 |
| 6 | 68.73 | CH | 3.78 td (8.6; 3.9) | 69.2 |
| 7 | 38.58 | $CH_2$ | 2.26; 1.84 | 38.4 |
| 8 | 46.79 | CH | 2.0 | 47.9 |
| 9 | 21.05 | C | - | 21.2 |
| 10 | 28.74 | C | - | 30.1 |
| 11 | 26.37 | $CH_2$ | 1.82; 1.44 | 26.6 |
| 12 | 34.20 | $CH_2$ | 1.85; 1.71 | 34.2 |
| 13 | 45.94 | C | - | 47.1 |
| 14 | 46.95 | C | - | 46.3 |
| 15 | 47.88 | $CH_2$ | 2.41 dd (2.7; 8.1); 1.28 | 47.8 |
| 16 | 74.19 | CH | 4.90 m | 74.6 |
| 17 | 60.89 | CH | 2.26 d (7.5) | 60.7 |
| 18 | 20.78 | $CH_3$ | 1.68 s | 21.0 |
| 19 | 30.32 | $CH_2$ | 0.20; 0.52 | 32.0 |
| 20 | 79.92 | C | - | 79.9 |
| 21 | 28.00 | $CH_3$ | 1.5 s | 28.3 |
| 22 | 26.68 | $CH_2$ | 3.12 td (13.9; 5); 1.26 | 26.4 |
| 23 | 24.07 | $CH_2$ | 2.20; 1.95 | 23.4 |
| 24 | 68.08 | CH | 3.60 dd (3.5; 2) | 69.4 |
| 25 | 75.30 | C | - | 75.9 |
| 26 | 28.61 | $CH_3$ | 1.45 s | 28.1 |
| 27 | 28.70 | $CH_3$ | 1.30 s | 28.0 |
| 28 | 19.17 | $CH_3$ | 1.0 s | 28.4 |
| 29 | 20.33 | $CH_3$ | 1.72 s | 15.5 |
| 30 | 16.74 | $CH_3$ | 1.52 s | 20.5 |
| | *β*-D-Glc*p* | | | |
| 1′ | 105.96 | | 4.92 d (13) | |
| 2′ | 79.0 | | 4.13 dd (9.3; 7.7) | |
| 3′ | 78.01 | | 4.24 | |
| 4′ | 72.50 | | 3.90 m | |
| 5′ | 78.10 | | 4.55 dd (11.7; 3.2) | |
| 6′ | 62.89 | | 4.45 dd (11.7; 4.5) | |
| | *α*-L-Rha*p* | | | |
| 1″ | 101.81 | | 5.70 d (8) | |
| 2″ | 72.17 | | 4.83 dd (4; 1.3) | |
| 3″ | 72.55 | | 4.70-4.44 (10.0) | |
| 4″ | 73.96 | | 4.39 t (10.0) | |
| 5″ | 69.63 | | 4.85 dq (10.6) | |
| 6″ | 18.72 | | 1.71 d (6.0) | |

Chemical shifts for C atoms in the $^{13}C$ NMR spectrum indicated that C-2 of the D-glucose was substituted [5]. The glucose H-6 atom resonated in the PMR spectrum as a doublet of doublets at 4.55 ppm. The resonances for C-5 and C-6 of the *β*-D-glucoside moiety were observed at 78.10 and 62.89 ppm, characteristic of a free $CH_2OH$ on D-glucose. The C-2 atom of this same sugar resonated at 79.92 ppm. These data show that L-rhamnose is the terminal sugar and is 1→2-bonded to D-glucose. Therefore, cycloascauloside B was a monodesmoside (Table 1). This was confirmed by C-5 of the aglycon appearing at 54.56 ppm as an isolated resonance that did not experience a $\beta$-effect of glycosylation at C-6. The same can be said about the C-7 resonance at 38.58 ppm [6-8].

Table 1 shows that C-3 of the aglycon had the greatest chemical shift (88.79 ppm) whereas those of C-6, C-16, and C-24 were unchanged. This means that the sugars were bonded to the C-3 hydroxyl as a biose.

Thus, cycloascauloside B had the structure 20*R*,25-epoxy-24*S*-cycloartan-3$\beta$,6$\alpha$,16$\beta$,24-tetraol 3-*O*-[$\alpha$-L-rhamnopyranosyl-(1→2)]-$\beta$-D-glucopyranoside.

## EXPERIMENTAL

The isolation and separation of triterpenoids from *A. caucasicus* have been reported [1, 2]. PMR and $^{13}$C NMR spectra in $C_5D_5N$ were obtained on Bruker AM-400 and DRX-500 instruments with TMS internal standard. $^{13}$C NMR spectra were recorded with full C–H decoupling and using DEPT and J-modulation. IR spectra in KBr disks were obtained on a UR-20 spectrometer.

**Cycloascauloside B (1)**, white crystalline powder, $C_{42}H_{70}O_{14}$, MW 798.250 (mass spectrometry). Table 1 gives the NMR spectra.

**Cyclocephalogenin (2).** Glycoside **1** (50 mg) was hydrolyzed by methanolic $H_2SO_4$ (10 mL, 0.5%), diluted with water, and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with water and evaporated. The solid was chromatographed over a column of silica gel with elution by $CHCl_3:CH_3OH$ (15:1) to isolate **2** (30 mg), mp 132-133°C ($CH_3OH$), which was identified by direct comparison with an authentic sample on TLC [8]. The aqueous part of the hydrolysate was neutralized, condensed, and chromatographed on paper using $C_5D_5N:C_6H_6:BuOH:H_2O$ (3:5:1:3). Comparison with standard samples detected D-glucose and L-rhamnose.

## REFERENCES

1. M. D. Alaniya, N. F. Chkadua, T. I. Gigoshvili, and E. P. Kemertelidze, *Khim. Prir. Soedin.*, 352 (2006).
2. M. D. Alaniya, N. Sh. Kavtaradze, T. I. Gigoshvili, S. Lavoi, A. Pichette, and V. V. Mshvildadze, *Khim. Prir. Soedin.*, 628 (2008).
3. M. D. Alaniya, M. I. Isaev, M. B. Gorovits, N. D. Abdullaev, E. P. Kemertelidze, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 332 (1983).
4. T. I. Gigoshvili, M. D. Alaniya, V. G. Tsitsishvili, R. Faure, L. Debrauwer, and E. P. Kemertelidze, *Khim. Prir. Soedin.*, 301 (2003).
5. M. I. Isaev, *Khim. Prir. Soedin.*, 528 (1992).
6. M. A. Agzamova and M. I. Isaev, *Khim. Prir. Soedin.*, 348 (1999).
7. I. Galis, H. A. Gazar, S. Piacente, and C. Pizza, *J. Nat. Prod.*, **64**, 1179 (2001).
8. M. D. Alaniya, M. I. Isaev, T. I. Gigoshvili, N. Sh. Kavtaradze, S. Lavoi, A. Pichette, and V. V. Mshvildadze, *Khim. Prir. Soedin.*, 299 (2007).