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TRITERPENE GLYCOSIDES AND THEIR GENINS FROM *Astragalus*. LXXXIV. SECOMACROGENIN B, A NEW 9,10-*seco*-CYCLOARTANE

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The structure of a new triterpenoid, secomacrogenin B, which was isolated from Astragalus macropus *Bunge (Leguminosae) roots and is 24*R*-9,10-*seco*-cycloartan-1(10),9(11)-dien-3*β*,7*β*,24,25-tetraol, was elucidated.*

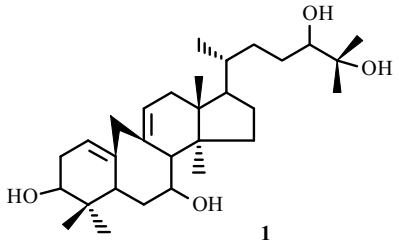
Keywords: *Astragalus macropus* Bunge, Leguminosae, cycloartane triterpenoids, cyclomacrogenin B, secomacrogenin B, PMR and ^{13}C NMR spectra, DEPT, ^{1}H–^{1}H COSY, HSQC, HMBC, NOESY.

In continuation of structural investigations of triterpenoids from *Astragalus macropus* Bunge (Leguminosae), we showed that the chromatographically homogeneous compound C [1] was not a pure compound. Rechromatography of this mixture over a column produced two fractions. The first contained a mixture of compounds. The second was a pure compound. Herein we present data on the structure elucidation of the latter, which we called secomacrogenin B (**1**).

The molecular formula of the new compound **1**, $C_{30}H_{50}O_4$, which was derived from NMR spectral data [1] and confirmed by quasi-molecular ions in positive- and negative-ion electrospray mass spectra (ESI-MS and ESI-MS), indicated that it was triterpenoid in nature. An examination of PMR and ^{13}C NMR spectra confirmed this conclusion (Table 1) and indicated that all O atoms were hydroxyls, three of which were secondary and one of which was tertiary. Therefore, **1** had six degrees of unsaturation. Because **1** contained two double bonds, it should have consisted of four rings, which is one ring less than for cycloartane triterpenoids. The PMR and ^{13}C NMR spectra indicated that the cyclopropane ring was missing and that seven methyls were present. Therefore, **1** was not a lanostane or cucurbitane triterpenoid, which are biologically related to cycloartanes [2]. In other words, **1** retained the 9,19- and 10,19-bonds. That meant that the 9,10-bond had been lost and, therefore, the new triterpenoid **1** was a 9,10-*seco*-cycloartane triterpenoid.

The PMR spectrum of **1** showed 1H doublets for an AX system of an isolated methylene at δ 2.77 and 3.03. The doublet at δ 2.77 in the HMBC spectrum had cross-peaks with four olefinic C atoms (δ 139.49, 135.82, 126.23, 117.17) and two methine C atoms that resonated at δ 44.99 and 55.74.

Because the last resonances belonged to C-5 and C-8, respectively, the isolated methylene was CH_2-19. Therefore, the double bonds were located on C-1–C-10 and C-9–C-11 and **1** had a 9,10-*seco*-cycloart-1(10),9(11)-diene C skeleton.



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The same PMR spectrum showed only one methyl group as a doublet. This defined the location of the tertiary hydroxyl as C-25.

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TABLE 1. Chemical Shifts of C and H Atoms and Parameters of DEPT, ^1H–^1H COSY, HSQC, HMBC, and NOESY Spectra of **1** ($CDCl_3$, δ, ppm, J/Hz)

C atom	DEPT	δ_C	δ_H	HMBC (C atom)	NOESY (H atom)
1	CH	117.17	5.30 dd (4.7, 2.4)	5	
2	CH_2	32.29	1.90, 2.30 dt (17.4, 6)		
3	CH	75.18	3.53 dd (9.6, 6)	29	29
4	C	38.16			
5	CH	44.99	1.72		
6	CH_2	35.94	1.82,		
			1.90	10	
7	CH	74.77	3.90 ddd (11.7, 7.4, 4.3)		28
8	CH	55.74	2.08 d (12)		
9	C	135.82			
10	C	139.49			
11	CH	126.23	5.40 d* (5.9)		
12	CH_2	37.55	1.96,	9, 11, 13, 14	
			2.06		
13	C	46.15			
14	C	48.34			
15	CH_2	35.74	1.50, 1.68		
16	CH_2	28.73	1.40, 1.96		
17	CH	50.83	1.60 q (9.6)		
18	CH_3	15.19	0.72 s	12, 13, 14, 17	
19	CH_2	45.41	(*a*) 2.77 d (14.4),	9, 10, 1, 11, 8, 5	19*b*, 1, 11
			(*b*) 3.03 d* (15)		19*a*
20	CH	36.33	1.41		
21	CH_3	18.70	0.91 d (6)	17, 20, 22	
22	CH_2	33.55	1.27, 1.50		
23	CH_2	28.81	1.38, 1.50		
24	CH	79.09	3.35 dd (6.5, 5.7)		
25	C	73.52			
26	CH_3	23.72	1.17 s	27, 24, 25	
27	CH_3	26.96	1.22 s	26, 24, 25	
28	CH_3	19.38	0.92 s	8, 13, 14, 15	7
29	CH_3	24.68	1.05 s	5, 4, 3	3
30	CH_3	13.79	0.73 s	5, 29, 4, 3	

*Doublets with broad components.

The PMR spectrum of **1** contained a 1H doublet at δ 2.08 with SSCC ^3J = 12 Hz that was assigned to H-8. The doublet splitting of this resonance indicated that a secondary hydroxyl located in ring B was situated on C-7, which was consistent with the chemical shift of C-8 (δ 55.31) [1].

The presence of axial–axial coupling constants (12 Hz) indicated that this hydroxyl had the β-equatorial orientation.

Methyls (CH_3-29 and CH_3-30) had cross-peaks in the HMBC spectrum with a secondary carbinol C atom that resonated at δ 75.18. Therefore, the secondary hydroxyl located on ring A was situated on C-3. The SSCC of the proton geminal to this hydroxyl, $^3J_1$ = 9.6 and $^3J_2$ = 6 Hz defined its orientation as α-axial. Therefore, the hydroxyl had the β-configuration.

The location of the remaining unidentified secondary hydroxyl was also determined from the HMBC spectrum. The carbinol C atom resonating at δ 79.09 in the HMBC spectrum had correlation peaks with methyls (CH_3-26 and CH_3-27). This fact defined unambiguously the location of the hydroxyl as C-24.

The chemical shift of C-24 (δ 79.09) defined the *R*-configuration for this asymmetric C atom [3]. This was confirmed by biogenetic considerations. Cyclomacrogenin B, which was isolated from this same plant, had a side chain identical to that of secomacrogenin B [1]. The chemical shifts of C-24 of cyclomacrogenin B at δ 79.06 (C_5D_5N) and of secomacrogenin B at δ 79.09 ($CDCl_3$) practically coincided despite the fact that these spectra were taken in different solvents.

Thus, secomacrogenin B had the structure 24*R*-9,10-*seco*-cycloarta-1(10),9(11)-dien-3β,7β,24,25-tetraol. Secomacrogenin B is the second representative of 9,10-*seco*-cycloartanes to be found in plants of the genus *Astragalus*. The first was prusianoside A, which was isolated from *A. prusianus* DC [4].

EXPERIMENTAL

General comments have been published [5]. We used the solvent system $CHCl_3$:CH_3OH 25:1.

NMR spectra were recorded in $CDCl_3$ on Inova 600 (Varian) and Unityplus-400 spectrometers. ^{13}C NMR spectra were taken with full C–H decoupling and under DEPT conditions. Two-dimensional spectra were recorded using standard Varian programs. Chemical shifts are given relative to TMS. IR spectra were recorded in KBr disks on a Bio-Rad FT-IR 165 Spectrometer. PI ESI MS and NI ESI MS were obtained in a Waters Alliance 2690-7Q 4000 spectrometer (LC/MS).

Isolation of Secomacrogenin B (1). Compound C [1] was rechromatographed over a silica-gel column with elution by the indicated system to produce a fraction (9 mg) with a mixture of compounds. The last fraction contained a pure compound (11 mg), secomacrogenin B (**1**).

Secomacrogenin B (1), $C_{30}H_{50}O4$. IR spectrum (KBr, ν_{max}, cm^{-1}): 3420 (OH), 1669, 1651 (>C=CH). ESI-MS (PI) *m*/*z*: 497.3 $[M + Na]^+$. ESI-MS (NI) *m*/*z*: 473.1 $[M - H]^-$. Table 1 gives the NMR spectra.

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