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TRITERPENE GLYCOSIDES AND THEIR GENINS FROM *Astragalus*. LXXIII. STEREOCHEMISTRY OF C-23 AND C-24 IN CYCLOARTAN- AND LANOSTAN-16β,23,24,25-TETRAOLS

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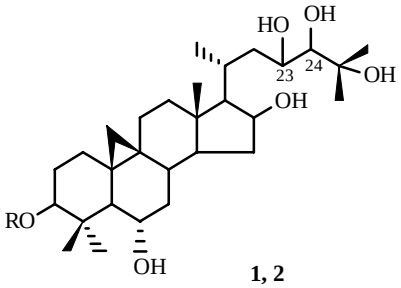
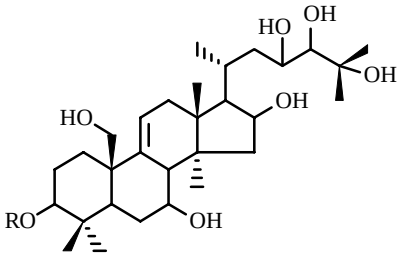
In continuation of structural studies of cycloartane and lanostane triterpenoids isolated from plants of the genus *Astragalus* (Leguminosae), we determined the stereochemistry of asymmetric C-23 and C-24 in cycloorbicoside D (**1**) as 23*R*,24*R* using an x-ray crystal structure [1]. The question of the absolute configuration of the same atoms in cycloorbigenin C (**2**) [2], orbigenin (**3**) [3], and orbicoside (**4**) [4] is also interesting and has not been answered. Herein we communicate a correlation between the PMR and ^{13}C NMR parameters and the absolute configuration of C-23 and C-24 in **1**-**4**.



1, 2



3, 4

1, 4: R = β-D-Xyl*p*; **2, 3:** R = H

Cycloorbigenin C is the genin of cycloorbicoside D and is produced from the latter by acid hydrolysis. Therefore, it has the same absolute configuration at C-23 and C-24 as cycloorbicoside D. As expected, the ^{13}C NMR spectra of **1** and **2** (Table 1) have chemical shifts for the asymmetric C atoms, δ 73.01 (73.17, chemical shifts of asymmetric atoms of **2** are given in parentheses) and 79.07 (79.19), that agree well.

Atoms H-23 and H-24 in the PMR spectrum of cycloorbicoside D resonate at δ 4.22 ppm as a multiplet and 3.67 as a doublet with J = 9 Hz, respectively (0 = HMDS) [5]. The PMR spectrum of cycloorbigenin C has signals for these protons at δ 4.33 as a triplet with broad lines and J = 8.5 Hz and at 3.77 as a doublet with J = 8.2 Hz, respectively (0 = TMS) [2, 5]. It can be seen that the parameters for H-23 and H-24 in the PMR spectra of **1** and **2** are practically identical if the difference in the chemical shifts of HMDS and TMS in C_5D_5N ($\Delta\delta$ = 0.12) is taken into account.

The good agreement of the chemical shifts for H-23, H-24, C-23, and C-24 in the PMR and ^{13}C NMR spectra of **1** and **2** with those of lanostane triterpenoids **3** and **4** is noteworthy.

Thus, signals for H-23 and H-24 in the PMR spectrum of orbigenin appear at δ 4.32 ppm (td, J = 8.5, 3.4 Hz) and 3.78 (d, J = 8.5 Hz) [3]. These same signals are observed in the PMR spectrum of orbicoside at δ 4.32 (td, J = 8.4, 3 Hz) and 3.78 (d, J = 8.4 Hz) [4]. These parameters are identical for orbigenin and orbicoside and practically the same as those of cycloorbigenin C and cycloorbicoside D. Also, the chemical shifts of C-23 and C-24 for **3** and **4** are δ 73.21 (73.20, shifts for **4** are given in parentheses) and 79.13 (79.14), which is in full agreement with the corresponding values in the ^{13}C NMR spectra of **1** and **2**.

Thus, we are correct in concluding that cycloorbigenin C, orbigenin, and orbicoside have the same 23*R*,24*R* stereochemistry as cycloorbicoside D.

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TABLE 1. Chemical Shifts of C Atoms of Cycloorbicoside D (**1**), Cycloorbigenin C (**2**), Orbigenin (**3**), and Orbicoside (**4**) (δ, ppm, C_5D_5N, 0 = TMS, with the exception of **1**, where 0 = HMDS)*

C atom	Compound			
	1	**2**	**3**	**4**
1	32.43	32.85	30.99	30.87
2	29.17	31.49	28.66	27.22
3	88.67	78.41	78.20	88.87
4	42.80	42.51	39.71	39.84
5	53.98	54.01	50.34	50.44
6	67.87	68.29	32.22	31.85
7	38.30	38.62	71.84	71.79
8	46.90	47.19	50.87	50.87
9	21.24	21.30	142.01	141.86
10	30.26	29.64	45.30	44.93
11	26.16	26.36	121.57	121.58
12	32.95	33.05	37.54	37.54
13	45.57	46.18	45.37	45.37
14	46.72	46.90	45.38	45.37
15	47.70	47.78	49.56	49.52
16	72.07	72.20	72.63	72.63
17	57.34	57.51	55.50	55.50
18	18.70	18.94	15.72	15.69
19	30.00	30.11	60.54	60.54
20	27.25	27.41	27.42	27.42
21	20.15	20.36	20.47	20.47
22	42.64	42.97	43.03	43.03
23	73.01	73.17	73.21	73.20
24	79.07	79.19	79.13	79.14
25	74.27	74.37	74.24	74.25
26	24.54	24.70	24.69	24.70
27	28.80	28.98	28.90	28.89
28	20.04	20.25	19.28	19.28
29	28.77	29.41	29.18	28.57
30	16.62	16.20	17.70	18.10
		β-D-Xyl*p*		
1	107.48			107.73
2	75.51			75.48
3	78.39			78.60
4	71.17			71.23
5	66.93			67.14

*For a correct comparison, the difference in the chemical shifts of HMDS and TMS in C_5D_5N ($\Delta\delta = 0.12$) should be added to the values in column 1.

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