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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS LVIII. THE STRUCTURE OF DIHYDROCYCLOORBIGENIN A

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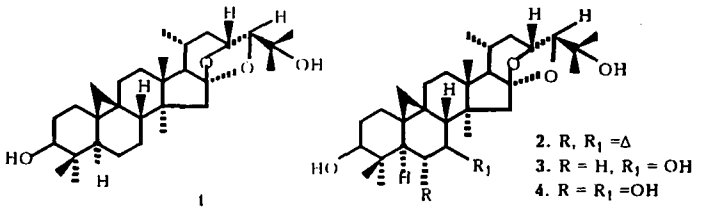
The herbage of the plant Astragalus orbiculatus *Ledeb. (Leguminosae) has yielded the new cycloartane triterpenoid dihydrocycloorbigenin A, which has the structure of (23R,24S)-16β,23; 16α,24-diepoxycycloartane−3β,25-diol.*

Continuing the study of *Astragalus orbiculatus* Ledeb. (Leguminosae) [1], from a methanolic extract of the herbage of this plant we have isolated a new glycoside, corresponding to substance (**5**) [2]. Its acid hydrolysis gave the genin (**1**), which we have called dihydrocycloorbigenin A.



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2. R, R_1 =Δ
3. R = H, R_1 = OH
4. R = R_1 =OH

From a consideration of the ^1H and ^{13}C NMR spectra (Table 1), the interpretation of which was made on the basis of the results of DEPT, $^1H-^1H$ COSY, HMQC, and HMBC experiments, the compound under study, (**1**), was assigned to the triterpenoids of the cycloartane series [3, 4].

In the PMR spectrum of genin (**1**), a one-proton doublet (^3J = 1 Hz) and a doublet of doublets of doublets ($^3J_1$ = 9; $^3J_2$ = 1.5; $^3J_3$ = 1 Hz) resonated at 3.72 and 4.79 ppm, these being characteristic for diepoxycycloartanes containing a ketal system with the ketal carbon atom C-16 and the C-23 and C-24 atoms bound to it. In the heteronuclear correlation (HMQC) spectrum the signals under consideration correlated with signals at 90.60 and 71.83, respectively. As was to be expected, in the weak-field part of the ^{13}C NMR spectrum of dihydrocycloorbigenin A the signal of a ketal atom was observed at 114.87 ppm.

In the IR spectrum of compound (**1**), with the composition $C_{30}H_{48}O_4$, an absorption band was observed at 3449 cm^{-1} that is characteristic of hydroxy groups. In agreement with this, the ^{13}C NMR spectrum of this compound showed two signals, at 77.93 and 71.01 ppm from secondary and tertiary alcoholic carbon atoms, respectively.

The good agreement of the chemical shifts of H-23 and H-24, and also of C-16, C-23, and C-24, with those of cycloorbigenin (**3**) [2] and cycloorbigenins A (**2**) [1] and B (**4**) [5] showed that the tertiary hydroxy group was present at C-25 and that the stereochemistries of the asymmetric centers of the side chains of these were identical.

The maximum peak of an anion with m/z 413 in the mass spectrum of dihydrocycloorbigenin A (scheme), arising on the cleavage of the C-24−C-25 bond, confirmed the conclusion that the tertiary hydroxy group was located at C-25. The same conclusion followed from the multiplicities of the signals of H-24 and of the 26- and 27-methyl groups in the spectrum of compound (**1**). The ion with m/z 332 observed in the same spectrum arises as a consequence of the splitting out of ring A and is characteristic for cycloartanes unsubstituted in rings B and C. The appearance of this ion showed that the secondary hydroxy group was located in ring A.

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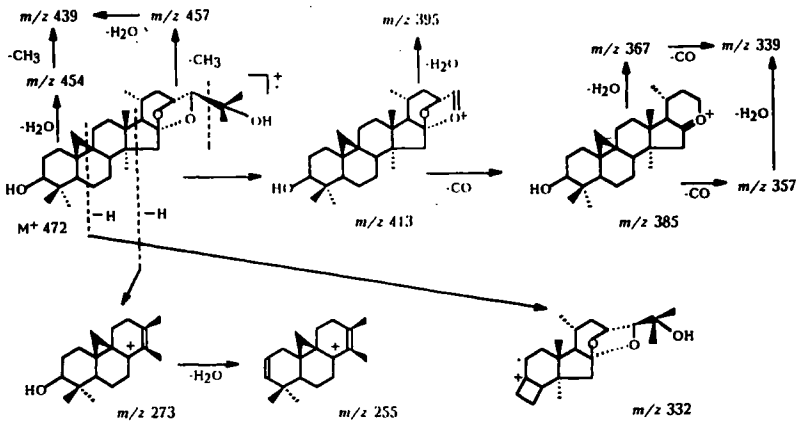
TABLE 1. Parameters of the ^{1}H, ^{13}C $^{1}H-^{1}H$ COSY, DEPT, HMQC and HMBC NMR Spectra of Compounds (**1-4**) (δ, ppm; 0 — TMS)

Atom C	Compound						
	1				**2**	**3**	**4**
	δ_C	DEPT	δ_H, J (Hz)	HMBC (C atoms)	δ_C		
1	32.41	CH_2	β 1.24		30.90	32.34	32.72
			α 1.57				
2	31.31	CH2	β 1.92 dtd (13; 11.4; 4)	1.3	30.05	31.22	31.68
			α 2.02	1.3			
3	77.93	CH	3.57 dd (11.4; 4.5)	29.30	77.33	77.94	78.05
4	41.15	C	-		40.85	40.93	42.46
5	47.44	CH	1.34 dd (12.5; 4.2)		43.46	46.57	51.67
6	21.30	CH_2	β 0.80 qd (12.5; 2.3)	5.7	128.87	32.18	72.88
			α 1.60	7			
7	26.75	CH_2	1.15, 1.34		127.52	70.35	75.00
8	47.79	CH	1.54		47.15	55.46	53.58
9	19.51	C	-		18.80	19.78	19.53
10	27.01	C	-		28.75	27.64	29.03
11	26.66	CH_2	1.15		25.35	26.96	26.61
			2.07	10.19			
12	33.11	CH_2	1.58; 1.68		33.77	33.24	32.97
13	44.59	C	-		44.44	44.34	44.19
14	46.32	C	-		46.41	46.97	46.75
15	46.62	CH_2	2.05; 2.10d (14)	13; 14; 16; 28	46.77	48.93	48.84
16	114.87	C	-		114.60	115.27	115.15
17	61.20	CH	1.60 d(11)	12;15;16; 18; 20;21	60.02	60.70	60.59
18	19.33	CH_3	1.17 s	12;13;14;17	17.33	19.01	18.72
19	30.75	CH_2	0.33;0.58 d (4)	1; 8; 9; 11	20.94	30.00	31.37
20	23.95	CH	170 tdq (11;7;6.4)	17;21	23.73	23.89	23.61
21	19.83	CH_3	0.87 d (6.4)	17;20;22	20.32	20.17	19.97
22	38.25	CH_2	β 2.28 ddd (13; 9; 7)	17; 20; 23; 24	38.16	38.52	38.34
			α 1.02 ddd (13; 11; 1.5)	20;21;24			
23	71.83	CH	4.79 ddd (9;1.5;1)	16; 20; 25	71.96	71.87	71.73
24	90.60	CH	3.72 d (1)	16;22;26;27	90.44	90.57	90.52
25	71.01	C	-		70.98	71.16	71.01
26	27.91	CH_3	1.53 s	24; 25; 27	27.84	27.80	27.95
27	24.77	CH_3	1.46 s	24; 25; 26	24.73	24.83	24.64
28	19.41	CH_3	1.25 s	8;13;14	16.08	19.10	19.28
29	26.22	CH_3	1.25 s	3; 4; 5; 30	26.19	26.25	29.15
30	14.90	CH_3	1.13 s	3; 4; 5; 29	15.23	14.80	16.00

Note. The chemical shifts of the protons given without multiplicities and SSCCs were determined from the $^{1}H-^{1}H$ COSY and HMQC spectra.



Mass spectrometric fragmentation of dihydrocycloorbigenin A(1)

In the HMQC spectrum the signal of the secondary carbinol carbon atom correlated with a doublet of doublets at 3.57 ppm ($^3J_1$ = 11.4; $^3J_2$ = 4.5 Hz). The parameters of these signals determined the position of the secondary hydroxy group at C-3 and its β-orientation.

Consequently dihydrocycloorbigenin A is (23R,24S)-16β,23;16α,24-diepoxycycloartane−3β,25-diol.

EXPERIMENTAL

For general observations, see [6]. We used the following solvent systems: 1) chloroform−methanol−water (70:12:1), 2) chloroform−methanol (20:1).

The ^1H and ^{13}C NMR spectra, the 2M NMR $^1H-^1H$ and $^1H-^{13}C$ chemical shift correlations ($^1H-^1H$ COSY, $^1H-^{13}C$ COSY, or HMQC) and the 2M NMR correlations of long-range $^1H-^{13}C$ couplings (HMBC) were obtained on UNITY Plus 400 and Bruker AM 400 instruments in deuteropyridine (δ, ppm; 0 — TMS). DEPT experiments were also used for the interpretation of the ^{13}C NMR spectra.

The isolation and separation of the triterpenoids of *Astragalus orbiculatus* were carried out as described in [2] and [7]. The fractions containing substance (**5**) that had accumulated in the isolation of cycloorbicosides A [7] and G [2] were rechromatographed on a column in system 1, with the isolation of 150 mg of the glycosidic substance (**5**).

Dihydrocycloorbigenin A (1). Substance (**5**) (40 mg) was hydrolyzed with 7 ml of 0.25% methanolic sulfuric acid at 40°C for 7 h. The reaction mixture was treated with 6 ml of water, and the methanol was evaporated. The precipitate that deposited was filtered off and dried. The dry residue was chromatographed on a column with elution by system 2, giving 9 mg of the genin (**1**), $C_{30}H_{48}O_4$, mp 237-238°C (from methanol). IR spectrum (KBr, ν, cm^{-1}): 3449 (OH), 3040 (CH_2 of a cyclopropane ring).

Mass spectrum, m/z (%): M+472(7.9), 457(33.8), 454(20.0), 439(36.9), 413(100), 395(23.1), 385(20.0), 367(10.8), 357(10.8), 353(4.6), 332(10.0), 315(13.8), 313(6.2), 299(9.2), 273(95.4), 271(7.7), 261(18.5), 259(15.4), 255(63.1), 251(13.8). For the ^1H and ^{13}C NMR spectra, see Table 1.

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