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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS
LVII. THE STRUCTURE OF CYCLOPYCNANTHOGENIN

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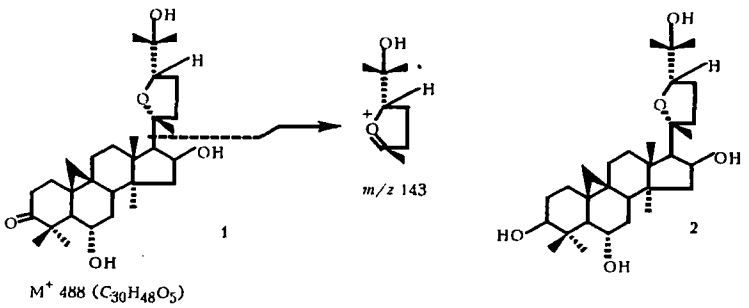
A new cycloartane methysteroid cyclopycnanthogenin, has been found in stems of the plant Astragalus pycnanthus *Boriss. (Leguminosae). Its structure has been determined on the basis of IR, mass, and ^1H and ^{13}C NMR spectra with the involvement of DEPT experiments and 2M $^1H-^1H$ and $^1H-^{13}C$ chemical shift correlations [$^1H-^1H$ COSY and $^1H-^{13}C$ (HMQC)] and also 2M NMR correlations of long-range $^1H-^{13}C$ interactions (HMBC). Cyclopycnanthogenin is 6α,16β,25-trihydroxy-20R,24S−epoxycycloartane-3-one.*

Continuing investigations of cycloartane methylsteroids from plants of the *Astragalus* genus we have determined the structure of substance B isolated from *A. pycnanthus*, which we have called cyclopycnanthogenin (**1**) [1].

The presence in the PMR spectrum of the new genin (**1**) of two one-proton doublets of an AB system at 0.37 and 0.69 ppm (Table 1) and also of the signals of seven methyl groups in a high field enabled us to assign the compound under study to the triterpenoids of the cycloartane series [2, 3].

The elementary composition of genin (**1**) is $C_{30}H_{48}O_5$. The mass spectrum of this compound showed the maximum peak of an ion with m/z 143. This fact, in combination with the presence in the PMR spectrum of a doublet of doublets at 3.90 ppm ($^3J_1$ = 9; $^3J_2$ = 5.4 Hz), assigned to H-24, showed that cyclopycnanthogenin had a side-chain similar to that of cyclosieversigenin (**2**) and of 20,24-epoxycycloartanes closely related to it [3-10]. The agreement of the chemical shifts of the C-20−C-27 carbon atoms with those of the corresponding atoms of cyclosieversigenin showed that the stereochemistries of the asymmetric carbon atoms of the side chains of the two compounds were also identical. This conclusion was confirmed by the signals of one of the C-22 protons, observed at 3.13 ppm in the form of a triplet of doublets ($^2J = {}^3J_1$ = 11.5 Hz; $^3J_2$ = 8.8 Hz) [3].



In the IR spectrum of cyclopycnanthogenin we observed an intense band of a six-membered cyclic ketone at 1706 cm^{-1}. Corresponding to this, in the ^{13}C NMR spectrum of the compound we traced the resonance lines of a ketonic carbon atom at 216.82 ppm. The chemical shift of the latter agreed well with those of the carbonyl carbon atoms of the 3-keto-cycloartanes cycloasgenins A [5] and B [11], and of 3-dehydrocycloasgenin C (**3**) [3]. This fact permitted the conclusion that the ketonic function of cyclopycnanthogenin involved the C-3 atom. In actual fact, in the same spectrum the signals of the C-2 and C-4 carbon atoms were shifted downfield and appeared at 35.86 and 50.56 ppm, respectively. In agreement with this conclusion, the PMR spectrum of cyclopycnanthogenin lacked the signal of a proton geminal to an OH group at C-3.

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TABLE 1. Chemical Shifts of the Carbon Atom and Protons, and Multiplicities and SSCCs (J, MHz) of the Latter in the ^1H and ^{13}C NMR Spectra of Cyclopycnanthogenin (1). Details of the 2M NMR $^1H-^1H$ and $^1H-^{13}C$ Chemical Shift Correlations ($^1H-^1H$ COSY and $^1H-^{13}C$ COSY or HMQC) and also the 2M NMR Spectra of Long-range Heteronuclear Interactions (HMBC). Chemical Shifts of the Carbon Atoms of Cyclosieversigenin (2) and 3-Dehydrocycloasgenin C (3) (δ, ppm, C_5D_5N; 0–TMS)

C atom	Compound				
	1			2	3
	δ_C	δ_H (J, Hz)	HMBC (C atoms)	δ_C	δ_C
1	31.85	1.30; 2.02	2; 9; 10; 19	32.81	31.91
2	35.86	α 2.48 ddd (14;6.8;1.2) β 2.75ddd (14; 8.4; 5.7)	1; 3; 29 1; 3; 29	31.47	35.88
3	216.82	-		78.32	216.77
4	50.56	-		42.46	50.57
5	53.55	2.23 d (10)	4;6;19;29;30	54.00	53.63
6	69.17	3.69 tdd (10;3.9; 2.9) [(OH) 5.68 d (3.9)]		68.38	69.21
7	38.39	α 1.61 td (11.6; 10) β 1.76 ddd (11.6; 3.6;2.9)		38.85	38.30
8	48.19	1.85 dd (11.6; 3.6)		47.30	48.29
9	21.21	-		20.99	21.50
10	28.49	-		29.92	28.28
11	26.07	0.99 ddd (13;10; 3) 2.05	9; 10; 19	26.32	26.23
12	33.20	1.64; 164	18	33.47	33.03
13	45.00	-		45.09	45.67
14	46.06	-		46.21	46.83
15	47.04	1.76; 2.12 dd (12.7; 8)	13; 17; 28	46.81	49.18
16	73.41	5.05 qd (8;2.9) [(OH) 5.59 d (2.9)]	13 15; 16	73.48	71.67
17	58.50	2.54 d (8)	12; 13; 16; 18; 20; 21; 22	58.44	57.35
18	22.14	1.43 s	12; 13; 17	21.66	18.72
19	31.08	0.37; 0.69 d (4)	1; 8; 5; 9; 10; 11	31.02	30.73
20	87.22	-		87.27	31.56
21	28.57	1.34 s	17	28.59	19.70
22	34.93	3.13 td (11.5; 8.8) 1.70 ddd (11.5; 9.8; 2.4)	20; 21; 23	34.97	29.35
23	26.45	2.07; 2.34 m	17	26.17	34.79
24	81.73	3.90 dd (9.5; 5.4)	25	81.75	80.55
25	71.27	(OH) 6.69 s	24; 25; 26; 27	71.27	72.68
26	27.18	1.32 s	24; 25	27.17	25.94
27	28.22	1.61 s	23; 24; 25	28.21	26.16
28	20.43	0.97 s	8; 13; 14; 15	20.27	20.43
29	28.65	1.78 s	3; 4; 5; 30	29.44	28.60
30	20.45	1.48 s	3; 4; 5; 29	16.14	20.55

Note. The chemical shifts protons given without multiplicities and SSCCs were determined from $^1H-^1H$ COSY and HMQC spectra. The multiplicity and SSCC of 2H-7 were determined from a difference spectrum obtained as a consequence of a double-resonance experiment with suppression of H-6, where H-7β was observed in the form of a doublet of doublets ($^2J = 11.6$, $^3J = 3.6$ Hz) and H-7α in the form of a triplet ($^2J = {}^3J = 11.6$ Hz).

Thus, of the five oxygen atoms one is a component of a carbonyl function and another is part of an epoxide function, while a third forms a tertiary hydroxy group. Taking this into account, it follows from the elementary composition of genin (1), $C_{30}H_{48}O_5$, that the two oxygen atoms remaining unidentified must be involved in hydroxy groups present in the polycyclic part of the molecule. In agreement with this, the PMR spectrum of genin (1) showed one-proton signals at 5.59, 5.68, and 6.69 ppm from the protons of hydroxy groups. The first signal was a singlet and related to the proton of a tertiary hydroxy group, while the other two had splitting of a doublet nature. Consequently, the corresponding hydroxy groups were secondary. As was to be expected, in the PMR spectrum under discussion the resonance lines of protons geminal to hydroxy groups were clearly traced at 3.69 (tdd, 10, 3.9, 2.9 Hz) and 5.05 ppm (qd, 7.8, 2.9 Hz). These parameters agree well with

the analogous parameters of 6β-H and 16α-H, respectively [3]. This meant that cyclopycnanthogenin contained 6α- and 16β-hydroxy groups. This conclusion was confirmed by the ^{13}C NMR spectrum of this genin, which contained the signals of secondary carbinol carbon atoms at 69.17 and 73.41 ppm. The downfield shift of the signal of the 4α-methyl group to 1.78 ppm may serve as an additional confirmation of the presence of a 6α-hydroxy group in the cyclopycnanthogenin molecule.

Thus, the spectral characteristics presented permit us to determine cyclopycnanthogenin as 6α,16β,25-trihydroxy-−20R,24S-epoxycycloartane-3-one.

EXPERIMENTAL

For general observations, see [12]. We used the following solvent systems: 1) chloroform−methanol (20:1), and 2) chloroform−methanol (15:1).

^1H and ^{13}C NMR spectra were taken on Bruker AM 400 and Unity Plus 400 instruments in deuteropyridine (δ, ppm, 0−TMS). The interpretation of the ^1H and ^{13}C NMR spectra was based on double-resonance, DEPT, ^1H-^1H COSY, HMQC, and HMBC experiments.

Cyclopycnanthogenin (1). Substance A isolated from *A. pycnanthus* [1] was repeatedly chromatographed on a column of silica gel in systems 1 and 2, and 12 mg (0.006%) of purified compound (**1**), $C_{30}H_{48}O_5$, mp 233-235°C was crystallized from methanol. IR spectrum (KBr, ν, cm^{-1}): 3415 (OH), 3040 (CH_2 of a cyclopropane ring), 1706 (C=O). Mass spectrum, m/z (%): M+ 488(0.4), 473(2.0), 470(3.8), 455(2.8), 452(2.1), 437(2.1), 429(2.1), 427(1.9), 419(0.8), 411(9.6), 393(9.6), 375(1.9), 369(3.6), 143(100), 125(61.5).

For the ^1H and ^{13}C, $^1H-^1H$, COSY, HMQC, and HMBS NMR spectra, see Table 1.

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