Chemistry of Natural Compounds, Vol. 33, No. 6, 1997

TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS

LV. STRUCTURE OF CYCLOORBIGENIN A

M. A. Agzamova and M. I. Isaev

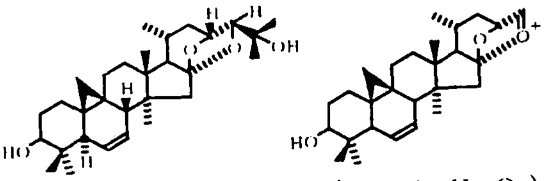
UDC 547.918:547.926

The structure of the new cycloartane triterpenoid cycloorbigenin A, isolated from Astragalus orbiculatus, *has been established on the basis of spectral characteristics. Cycloorbigenin A is (23R,24S)-16β,23:16α,24-di-epoxycycloart-6-ene-3,25-diol.*

Continuing a study of isoprenoids of the plant *Astragalus orbiculatus* Ledeb. (Leguminosae) [1-5], from the products of the hydrolysis of a fraction containing both cycloorbicoside A and a new glycoside, we have isolated a new genin, which we have called cycloorbigenin A (**1**).

The ^{1}H NMR spectrum of (**1**) contained the signals of one-proton doublets of an *AB* system ($^2J = 4$ Hz) at −0.14 and 0.82 ppm, showing the presence of a 1,1,2,2-tetrasubstituted three-membered ring, and seven methyl groups in the high field, showing that cycloorbigenin A was a methylsteroid of the cycloartane series [6, 7]. An absorption band at 3035 cm^{-1} in the IR spectrum of the new compound (**1**) agreed with the assignment of the compound concerned to the cycloartane triterpenoids.

In the PMR spectrum of cycloorbigenin A at 4.72 and 3.63 ppm there was a one-proton doublet with broadened lines having $^3J = 8.4$ Hz and a one-proton singlet, which were ascribed to H-23 and H-24, respectively. These facts, in combination with the mass spectrum of genin (**1**), which contained the peak of the maximum ion *a* with *m/z* 411 ($C_{27}H_{30}O_3$) showed that this genin had a side-chain similar to that of cycloorbigenin and cycloorbigenin B. The ion *a* arises on the elimination of a hydroxyisopropyl fragment through cleavage of the C-14−C-25 bond [1, 4].



1

a *m/z* 411($C_{27}H_{39}O_9$)

The signals of the ketalic carbon atom, C-16, and of the carbon atoms C-23 and C-24 linked to the ketalic oxygen atoms were detected at 114.60, 71.96, and 90.44 ppm and showed the identity of the stereochemistries of the chiral centers under discussion with those of cycloorbigenin and cycloorbigenin B [3, 5].

The elementary composition of the genin was $C_{30}H_{46}O_4$. Consequently, two oxygen atoms formed the ketal system and one was in the tertiary hydroxy group at C-25. The presence of the signals of a secondary carbinol carbon atom in the ^{13}C NMR spectrum at 77.38 ppm showed that the fourth oxygen atom formed a β-oriented hydroxy group at C-3. A confirmation of this was a one-proton doublet of doublets at 3.51 ppm with the SSCCs $^3J_1 = 11$ Hz and $^3J_2 = 4.5$ Hz in the PMR spectrum of genin (**1**), relating to a proton geminal to a secondary hydroxy group.

It followed from the elemental composition of substance (**1**) that there had to be one double bond in the molecule. The chemical shifts of the sp^2-hybridized carbon atoms (128.87 and 127.52 ppm) confirmed the presence of a disubstituted π-bond. In agreement with this, as was to be expected, the PMR spectrum of this compound showed the signals of two olefinic protons

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (3712) 40 64 75. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 848-850, November-December, 1997. Original article submitted April 21, 1997.

0009-3130/97/3306-0663$18.00

TABLE 1. Chemical Shifts of the Carbon Atoms of Cycloorbigenin A (1)

C atom	ppm	C atom	ppm	C atom	ppm
1	30.90	11	25.35	21	20.32
2	30.05	12	33.77	22	38.16
3	77.33	13	44.44	23	71.96
4	40.85	14	46.41	24	90.44
5	43.16	15	46.77	25	70.98
6	128.87	16	116.60	26	23.73**
7	127.52	17	60.02	27	24.73**
8	47.15	18	17.33	28	16.08
9	18.80	19	20.94	29	26.19
10	28.75	20	27.84	30	15.23

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*Signals labeled with asterisks have been assigned ambiguously.

at 5.45 and 5.75 ppm as components of an allyl spin system. The latter could be present in ring *B* of the cycloorbigenin A molecule. Consequently, the double bond was located at C-6. The upfield shift of the signal of one of the methylene protons of the cyclopropane fragment to −0.14 ppm and of the signal of the corresponding carbon atom (C-19) to 20.94 ppm in the ^{1}H and ^{13}C NMR spectra of cycloorbigenin A was a consequence of the influence of the Δ^6-double bond and served as an additional proof of the position of the latter [8].

Thus, cycloorbigenin A has the structure (23R,24S)-16β,23:16α,24-diepoxycycloart-6-ene-3,25-diol.

EXPERIMENTAL

For general observations, see [1]. ^{1}H and ^{13}C NMR spectra were taken on a Bruker AC 200 instrument in deuteropyridine with TMS as internal standard (δ, ppm). ^{13}C NMR spectra were also obtained under J-modulation conditions.

Cycloorbigenin A (1) and Cycloorbigenin. The fraction (500 mg) containing cycloorbicoside and a new glycoside that accumulated in the isolation of cycloorbicoside A was hydrolyzed with 200 ml of a 0.5% methanolic solution of sulfuric acid. After the usual work-up, the genin part of the reaction product was chromatographed on a column of silica gel, with elution by the chloroform–methanol (20:1) system. In this way, 50 mg of cycloorbigenin A (1) and 210 mg of cycloorbigenin [1] were isolated.

Cycloorbigenin A (1), $C_{30}H_{46}O_4$, mp 207-209° (from the $CHCl_3$–MeOH (20:1) system), $[\alpha]_D^{18}$ −101.3 ± 2$^\sigma$ (*c* 0.75; MeOH). IR spectrum (KBr, ν, cm^{-1}): 3500-3340 (OH), 3035 (CH_2 of cyclopropane ring). Mass spectrum, *m/z* (%): M^+ 470(100), 455(32.5), 452(32.5), 437(22.5), 411(100), 393(25.0), 253(25.0). PMR spectrum: −0.14 and 0.82 (2H-19, d, $^2J=4$ Hz), 0.81 (CH_3-21, d, $^3J=6$ Hz), 1.00; 1.06; 1.10; 1.30; 1.39; 1.45 (6 × CH_3, c), 3.51 (H-3, dd, $J_{3,2a}$ = 11.0 Hz, $J_{3,2e}$ = 4.5 Hz), 3.63 (H-24, s), 4.72 (H-23, d, $^3J=8.4$ Hz with broadened lines), 5.45 (H-7, ddd, $J_{6,7}=10$ Hz, $J_{7,8}=5$ Hz, $J_{7,5}=3$ Hz), 5.75 (H-6, d, $^3J=10$ Hz, with broadened lines). For the ^{13}C NMR spectrum, see Table 1.

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