TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS

XLIII. CYCLOARALOSIDE B FROM Astragalus amarus

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The structure of a new cycloartane glycoside, cycloaraloside B, isolated from the roots of Astragalus amarus Pall. (Leguminosae) has been established on the basis of chemical transformations and spectral characteristics: it is 20R,24S-epoxycycloartane-3β,6α,16β,25-tetraol 3-O-[O-α-L-rhamnopyranosyl-(1→2)-(6-O-acetyl-β-D-glucopyranoside)].

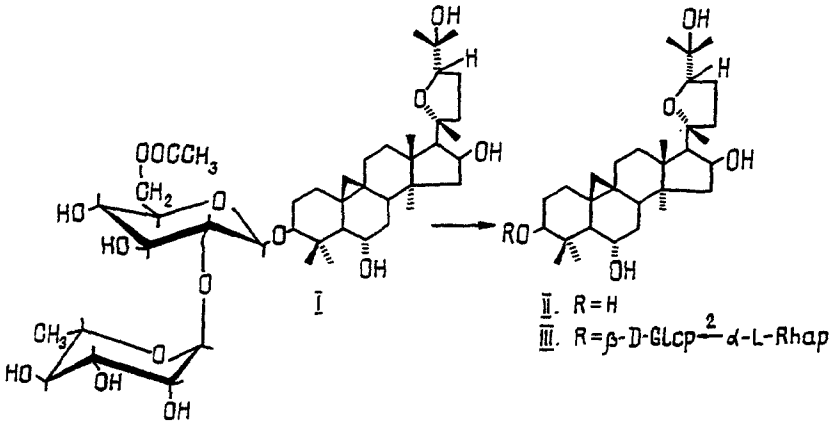
Completing a study of the cycloartanes of Astragalus amarus Pall. (Leguminosae), we have established the structure of substance (5) [1], which we have called cycloaraloside B (I).

In the PMR spectrum of cycloaraloside B, the protons of an isolated cyclopropane methylene resonated at 0.25 and 0.58 ppm. The acid hydrolysis of glycoside (I) led to cyclosieversigenin (II). These facts permitted the unambiguous assignment of the glycoside under consideration to the triterpenoids of the cycloartane series.

GLC [4] showed the presence in glycoside (I) of D-glucose and L-rhamnose residues in a ratio of 1:1.

The IR spectrum of glycoside (I) contained absorption bands at 1740 and 1260 cm^{-1}, which are characteristic for an ester group. The ^1H and ^{13}C NMR spectra, containing a three-proton singlet at 2.04 ppm and the signals of carbon atoms at 170.71 and 20.76 ppm, showed that cycloaraloside B was a monoacetate.

The alkaline hydrolysis of glycoside (I) gave cycloaraloside D (III) [5].



The position of the acetyl group in glycoside (I) was determined from a study of ^1H and ^{13}C NMR spectra (Tables 1 and 2).

The signals of the protons of the carbohydrate components of glycoside (I) were assigned unambiguously by the use of double homonuclear resonance. Among these signals, doublets of doublets at 4.75 and 4.83 ppm attracted attention, these being the AB part of an ABX system and belonging to H-6 and H-6' of a β-D-glucose residue. It must be mentioned that in the spectrum of glycoside (III) H-6' resonated in the form of a doublet of doublets at 4.55 ppm. A downfield shift of the H-6 and H-6' signals on passing from glycoside (III) to glycoside (I) showed that the acetyl group was located at C-6 of the β-D-glucopyranosyl residue of cycloaraloside B. A similar conclusion also followed from a comparative analysis of the

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TABLE 1. Chemical Shifts (δ; ppm), Multiplicities, and SSCCs (J, Hz) of the Protons of Cycloaraloside B (I) (C_5D_5N; O – TMS)

Protons of the genin part	Protons of the carbohydrate
H-3 3.54 dd (11; 4)	β-D-Glcp
H-6 3.76 td (9; 4)	H-1 4.92 d (8)
H-16 5.00 q (7.8; 7.8; 7.8)	H-2 4.28 t (8)
H-17 2.52 d (7.8)	H-3 3.92 m*
2H-19 0.25; 0.58 d (4)	H-4 4.35 t (6)
H-22 3.08 q (8; 8; 8)	H-5 3.92 m*
H-24 3.87 dd (10; 5.5)	H-6 4.75 dd (12; 6)
CH_3 groups	H-6′ 4.83 dd (12; 2)
1.01 s	Ac 2.04 s
1.28 s	α-L-Rhap
1.30 s	H-1 6.55 d (1.3)
1.40 s	H-2 4.79 dd (4; 1.3)
1.49 s	H-3 4.69 dd (10; 4)
1.56 s	H-4 4.31 t (10)
1.95 s	H-5 4.86 dq (10.6)
	3H-6 1.71 d (6)

*Signals superposed on one another.

TABLE 2. Chemical Shifts of the Carbon Atoms of Compounds (I-III) (δ, ppm; O – TMS; C_5D_5N)

C Atom	Compound			C Atom	Compound		
	I	II	III		I	II	III
1	32.65	32.72	32.72	24	81.68	81.57	82.03
2	29.47	31.30	30.25	25	71.20	71.19	71.19
3	89.14	78.21	88.55	26	28.13*	27.04*	27.08*
4	42.59	42.28	42.61	27	28.50*	28.09*	28.40*
5	54.25	53.86	54.31	28	20.11	20.17	20.23
6	67.87	68.27	67.99	29	28.05	20.28	28.69
7	38.47	38.69	38.36	30	16.70	16.16	16.71
8	46.85	47.21	46.96		β-D-Glcp residue		
9	20.86	20.84	21.03	1	105.35		105.09
10	30.25	29.80	29.66	2	79.60		79.57
11	26.21	26.29[a]	26.48	3	77.70		78.42
12	33.39	33.31	33.66	4	72.01		72.60
13	45.02	44.89	45.38	5	74.74		77.51
14	46.13	46.09	46.35	6	64.80		63.21
15	46.61	46.69	46.87		α-L-Rhap residue		
16	73.40	73.35	73.40	1	101.81		101.51
17	58.34	58.26	58.56	2	72.50		72.22
18	21.38	21.51	21.35	3	72.42		72.55
19	30.40	31.00	30.51	4	74.13		74.28
20	87.21	87.17	87.20	5	69.64		69.46
21	27.09	28.46	27.99	6	18.63		18.47
22	34.89	34.81	35.21	COO	170.71		
23	26.39	26.29[a]	26.34	CH_3	20.76		

Note: The signals marked by the same letters are superposed on one another, and the assignment of those marked with asterisks is uncertain.

^{13}C NMR spectra of cycloaralosides B (I) and D (III). In the spectrum of glycoside (III) the resonance lines of the C-5 and C-6 atoms in the β-D-glucopyranosyl residue were observed at 77.51 and 63.21 ppm. In the spectrum of glycoside (I) the same signals were traced at 74.74 and 64.80 ppm. The changes in the chemical shifts of these carbon atoms were due to the β- and α-effects, respectively, of an acetyl group located at C-6.

Thus, cycloaraloside B has the structure of 20R,24S-epoxycycloartane-3β,6α,16β,25-tetraol 3-O-[O-α-L-rhamnopyranosyl-(1→2)-(6-O-acetyl-β-D-glucopyranoside].

EXPERIMENTAL

For general observations, see [4]. The following solvent systems were used: 1) ethyl acetate–methanol (5:1); 2) chloroform–methanol (15:1); 3) chloroform–methanol–water (70:32:4).

^1H and ^{13}C NMR spectra were taken in deuteropyridine on Bruker AM-400 and Bruker WM-250 instruments (δ, ppm; 0 – TMS). ^{13}C NMR spectra were also obtained under the conditions of J-modulation.

For the isolation of cycloaraloside B, see [1].

Cycloaraloside B (I) – substance (5) [1], $C_{44}H_{72}O_{15}$, mp 181-183°C (from system 1); $[\alpha]_D^{24}$ 0 ± 3° (c 0.7; methanol); ν_{max}^{KBr} cm^{-1}; 3550-3310 (OH), 1740, 1260 (ester group). GLC [4] showed that cycloaraloside B contained D-glucose and L-rhamnose residues in a ratio of 1.00:0.86.

Cyclosieversigenin (II) from (I). Cycloaraloside B (45 mg) was hydrolyzed with 10 ml of a 0.5% methanolic solution of sulfuric acid at 60°C for 4 h. Then the reaction mixture was diluted with water and extracted with chloroform. The chloroform extract was washed with water and was evaporated. The residue was chromatographed on a column, with elution by system 2. This led to the isolation of 20 mg of cyclosieversigenin (II), mp 239-241°C (from methanol), $[\alpha]_D^{24}$ = 52 ± 2° (c 0.8; methanol), which was also identified by direct TLC comparison with an authentic specimen [3].

Cycloaraloside D (III) from (I). Cycloaraloside B (37 mg) was hydrolyzed with 5 ml of a 0.1% solution of sodium hydroxide at room temperature for 1 h. The reaction mixture was diluted with water and was treated with n-butanol. The butanolic extract was washed with water and evaporated. The reaction product was chromatographed on a column, with elution by system 3. This gave 30 mg of glycoside (III), mp 226-228°C (from methanol), $[\alpha]_D^{24}$ –12 ± 2° (c 0.7; methanol), which was identified as cycloaraloside D by the usual methods [5].

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ALKALOIDS OF Aconitum sajanense

II. STRUCTURE OF DEHYDROACOSANINE

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The new alkaloid dehydroacosanine has been isolated from the roots of Aconitum sajanense Kumin, and its structure has been established by spectral and chemical methods.

The isolation from the epigeal part of Aconitum sajanense Kumin of the new alkaloid acosanine, having the structure of 6-O-demethyldelphatine, has been reported previously [1]. In the present paper we give the results of a study of alkaloids from the roots of this plant gathered in Krasnoyarsk Territory (Ermakovskii region, Western Sajan mountains, Kedranskii range, environs of Lake Oiskoe, on the Abakan–Kyzyl trail, at a height of 1600 m above sea level).

Extraction of the roots with chloroform yielded the total alkaloids (1.78% of the weight of the dry roots), which were separated into nonpolar (hexane, ether, and chloroform) and polar (aqueous) fractions. By chromatography the hexane fraction yielded a base with mp 140-141°C (I), while the aqueous fraction yielded acosanine (II).

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