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TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS. XXXVIII. CYCLOALPIGENIN D AND CYCLOALPIOSIDE D FROM Astragalus alopecurus

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Eight compounds of triterpenoid nature have been isolated from the epigeal parts of the plant Astragalus alopecurus Pall. (Leguminosae) and have been designated in order of increasing polarity as substance 1—8. On the basis of chemical transformations and spectral characteristics, we have established the structures of 4 and 8, which have been called cycloalpigenin D and cycloalpioside D, respectively. Cycloalpigenin D is 20R,24S-epoxycycloartane-3β,7β, 16β,25-tetraol. Cycloalpioside D is cycloalpigenin D 3-O-β-D-xylopyranoside.

Continuing investigations of the cycloartane methylsteroids of plants of the genus Astragalus (Leguminosae) [1], we have begun a study of Astragalus alopecurus Pall. (foxtail milk vetch). In a methanolic extract of the epigeal part of the plant eight products of triterpenoid nature were detected in TLC, and these have been designated in order of increasing polarity as substances 1—8. Chromatography of the total triterpenoids and repeated rechromatography of the individual fractions on a column led to the isolation of the individual compounds 1—8. The first four substances consisted of genins, and the last four were of glycosidic nature. The present work was devoted to proving the structures of the new substances 4 and 8, which we have called cycloalpigenin D (I) and cycloalpioside D (V), respectively.

In the strong-field region of the PMR spectrum of cycloalpigenin D (Table 1), there were the signals of seven methyl groups and of two protons interlinked in the manner of an AB system, at 0.19 and 0.68 ppm with ^2J = 4 Hz, which are characteristic for an isolated cyclopropane methylene group. The presence of the latter was also shown by an absorption band at 3040 cm^{-1} in the IR spectrum of the compound under consideration [2]. The facts given, and also the molecular formula $C_{30}H_{50}O_5$, showed that the new genin (I) belonged to the triterpenoids of the cycloartane series [3, 4]. (see Scheme 1).

The acetylation of the genin (I) with acetic anhydride in pyridine led to the diacetate (II) and the triacetate (III). A comparative analysis of the PMR spectra of compounds (I-III) enabled the signals at 3.42, 3.70, and 4.97 ppm in the spectrum of the genin (I) to be assigned to protons located geminally to secondary hydroxy groups.

In the mass spectra of cycloalpigenin D (I) and its acetates (II) and (III) the maximum peak in each case was that of an ion with m/z 143 arising on the cleavage of the C-17—C-20 bond, while in the PMR spectra of the same compounds, one-proton signals were clearly seen at 3.78, 3.77, and 3.81 ppm, respectively, belonging to H-24. These facts indicated that

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TABLE 1. Chemical Shifts of the Protons of Cycloalpigenin D (I) and Its Derivatives (δ, ppm, O-HMDS)

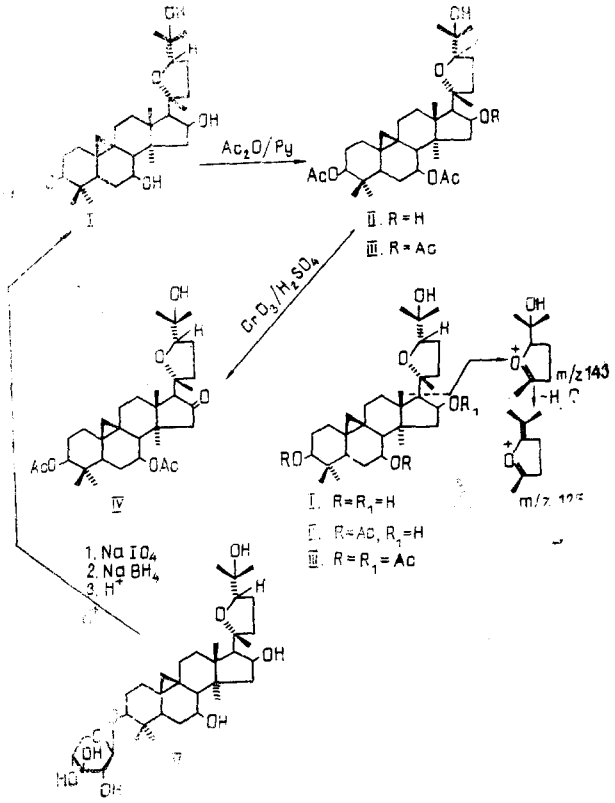
Compound	Positions of the protons								
	H-3	H-7	H-16	H-17	2H-19	H-22	H-24	CH_3 groups	OAc
I	3,42 dd ^3J=12; 4 Hz	3,70 m	4,97 q ^3J=7,3; 7,3 7,3 Hz	2,40 d ^3J=8 Hz	0,19; 0,68 d, ^2J=4 Hz	2,99 q ^2J=$^3J_1$= $^3J_2$=10 Hz	3,78 dd ^3J=8; 6 Hz	0,96; 1,0; 1,09; 1,18; 1,23; 1,41; 1,45	—
II	4,60 dd ^3J=12; 4 Hz	4,84 m*	4,84 m*	2,31 d ^3J=8 Hz	0,19; 0,59 d, ^2J=4 Hz	2,95 q ^2J=$^3J_1$= $^3J_2$=9,3 Hz	3,77 dd ^3J=8; 6 Hz	0,70; 0,80; 0,83; 1,20; 1,20; 1,34; 1,47	1,91; 1,94
	[4,50 m]*	[4,70 ddd ^3J=10; 10; 3 Hz]	[4,50 m]*	[2,15 dd ^3J=7,5 Hz]	[0,31; 0,73 d, ^2J=4Hz]	[2,50 q ^2J=$^3J_1$= $^3J_2$=10Hz]	[3,68t ^3J=7,5 Hz]	[0,80; 0,82; 0,85; 1,10; 1,19; 1,23; 1,23]	[1,95; 1,98]
III	4,55 dd ^3J=11; 5 Hz	4,76 ddd ^3J=11; 11; 3,5 Hz	5,42 m	2,37 d ^3J=8,5 Hz	0,23; 0,61 d, ^2J=4 Hz		3,81t ^3J=7 Hz	0,70; 0,82; 0,82; 1,24; 1,28 1,30; 1,30	1,88; 1,92; 1,97
	[4,59 m]	[4,65 ddd ^3J=10; 10; 4 Hz]	[5,25m]	[2,28 d ^3J=8 Hz]	[0,36; 0,68 d, ^2J=4 Hz]		[3,60 t ^3J=7,5 Hz]	[0,77; 0,80; 0,86; 1,01; 1,12; 1,23; 1,28]	[1,89; 1,93; 1,93]
IV	4,57 dd ^3J=10; 5 Hz	4,72 ddd ^3J=10; 10; 3 Hz	—	2,81 s	0,16; 0,57 d, ^2J=4 Hz		3,74 m	0,70; 0,82; 0,89; 1,15; 1,15; 1,16; 1,35	1,88; 1,92
	[4,46 m]	[4,70 ddd ^3J=10; 10; 3 Hz]	—	[2,74s]	[0,44; 0,74 d ^2J=4 Hz]		[3,65 t ^3J=7 Hz]	[0,80; 0,84; 1,05; 1,05; 1,15; 1,18; 1,18]	[1,93; 1,97]

The spectra were taken in deuteropyridine or deuterochloroform. The results given in square brackets were obtained with the use of deuterochloroform. Signals marked by asterisks in horizontal lines were superposed upon one another. The signals of methyl groups had a singlet nature. Abbreviations: s) singlet; d) doublet; t) triplet; q) quartet; m) multiplet.

TABLE 2. Chemical Shifts of the Carbon Atoms of Cycloalpigenin D (I) and of Cycloalpioside D (V) (δ, ppm, O-TMS)

C atom	Compound		C atom	Compound	
	I	V		I	V
1	32,12a	31,74a	19	29,36	28,83
2	31,07	29,88	20	87,25	87,25
3	77,76	88,22	21	28,61	28,61
4	40,78	40,93	22	35,03	34,96
5	46,39b	46,31b	23	26,44	26,67e
6	32,12a	31,74a	24	81,64	81,64
7	70,44	70,21	25	71,26	71,19f
8	55,35	55,05	26	27,04	27,04d
9	19,94c	19,94c	27	28,16	28,16
10	27,34	27,04d	28	19,94e	19,94c
11	26,74	26,67e	29	26,22	25,70
12	33,39	33,31	30	14,72	15,23
13	45,57	45,49		β-D-Xylp residue	
14	46,39b	46,31b	1		107,49
15	48,85	48,70	2		75,44
16	73,80	73,73	3		78,51
17	57,96	57,96	4		71,19f
18	21,36	21,21	5		67,0

The signals marked with the same letters within a column were superposed upon one another.



Scheme 1

genin (I) had a side chain similar to the side chains of cyclosieversigenin [4, 5], cycloasgenin A [4, 6], and cyclogalegigenin [4, 7].

Consequently, the three secondary hydroxy groups were present in the polycyclic moiet of the molecule, and one tertiary hydroxy group in the side chain.

The diacetate (II) was subjected to Jones oxidation [8]. In the IR spectrum of the resulting keto compound (IV) (M^+ 572), the absorption band of the keto function was superposed completely on the band of an ester group at 1745 cm^{-1}. This means that the keto function was present in a five-membered ring.

Ketone (IV) exhibited a negative Cotton effect on the CD curve at 305 nm ($\Delta\varepsilon = -4.06$). This fact unambiguously showed the position of the keto function in the compound (IV) under consideration, and of the secondary hydroxy group that had remained free in the diacetate (II), at C-16 [9].

The increment in molecular rotations between the triacetate (III) and the diacetate (II) {$[M]_{D\text{-III}} + 465.7°$; $[M]_{D\text{-II}} + 318.6°$; $\Delta[M]_{D(\text{III-II})} + 147.1°$} showed the β configuration of the hydroxy group at C-16 [10].

A comparison of the characteristics of the PMR spectra of genin (I) and its derivatives (II-IV) permitted a quartet at 4.97 ppm with a distribution of the intensity of its lines as 1:3:3:1 and the SSCCs $^3J_1 = {}^3J_2 = {}^3J_3 = 7.3$ Hz in the spectrum of compound (I) to be assigned to the proton geminal to the hydroxy group at C-16. The facts given agree well with those for 16α-H [4].

The good agreement of the parameters of the doublet of doublets at 3.42 ppm in the spectrum of cycloalpigenin D and the corresponding signals in the spectra of compounds (II-IV) with those for 3α-H [4] showed the presence of a 3β-hydroxy group.

As followed from the multiplicities of the H-3 and H-16 signals, the molecule of compound (I) under consideration lacked an α-diol grouping. In actual fact, cycloalpigenin D was not oxidized by sodium periodate.

The multiplet at 3.70 ppm in the spectrum of genin (I) belonged to a proton geminal to an unidentified secondary hydroxy group. The signal of the proton under discussion in the spectra of the acetates (II-IV) was shifted downfield and was observed in the form of a sextet with the SSCCs $^3J_1 = {}^3J_2 = 10$ and $^3J_3 = 3$ Hz. This proton may be present in ring B and occupy either the 6β or the 7α position. The choice in favor of the latter was made on the basis of the fact that in the spectrum of genin (I) taken in deuteropyridine the signal of the 4α-methyl group was not shifted downfield to 1.8 ppm [3-5]. Thus, the hydroxy group sought was located at C-7 and had the β orientation.

In the ^{13}C NMR spectrum, the carbon atoms bearing secondary hydroxy groups resonated at 77.76 ppm (C-3), 70.44 ppm (C-7), and 73.8 ppm (C-16). The chemical shifts of the C-3 and C-7 atoms agree well with those for cycloorbigenin [11, 12], which has analogous functions, and that of C-16 with the chemical shift of the corresponding atom of cyclosieversigenin [13]. These facts serve as an additional confirmation of the conclusion of the presence of 3β,7β,16β-hydroxy groups in the molecule of cycloalpigenin D.

The stereochemistry of the C-20 and C-24 asymmetric centers was deduced by a comparative study of the ^{13}C and ^1H NMR spectra of cycloalpigenin D and of 20,24-epoxycycloartane-16β, 25-diols [4]. The good agreement of the chemical shifts of all the carbon atoms (C-20–C-27) of the side chain of genin (I) with those of cyclosieversigenin showed the identity of the stereochemistries of the C-20 and C-24 chiral centers in the compounds compared.

The 20R,24S configuration of the asymmetric atoms of the side chain of cycloalpigenin D was also shown by the PMR spectrum of this compound, where the signal of one of the protons at C-22 was clearly traced in the form of a quartet with a distribution of the intensities of its lines as 1:3:3:1 and the SSCCs $^2J = {}^3J_1 = {}^3J_2 = 10$ Hz [4].

Thus, the experimental results given permitted us to conclude that cycloalpigenin D has the structure of 20R,24S-epoxycycloartane-3β,7β,16β,25-tetraol.

The presence in the PMR spectrum of cycloalpioside D (V) of two one-proton doublet AB systems at 0.13 and 0.63 ppm and also of the signals of seven methyls in the strong field permitted us to assign the glycoside under consideration, again, to the triterpenoids of the cycloartane series [3, 4]. As another confirmation of this we may give the fact that the acid hydrolysis and the Smith degradation of glycoside (V) [14] led to cycloalpigenin D (I).

It was shown by the PC and GLC methods that glycoside (V) contained a D-xylose residue. Quantitative analysis of the monosaccharide composition of cycloalpioside D with the aid

of GLC [15] in the presence of D-glucose as standard showed the presence of one D-xylose molecule.

A similar conclusion followed from the ^1H and ^{13}C NMR spectra of the new glycoside (V). In the PMR spectrum od cycloalpioside D there was the signal of one anomeric proton at 4.71 ppm in the form of a doublet with the SSCC ^3J = 7 Hz, likewise showing the β configuration of the glycosidic bond and the C1 conformation and pyranose form [13] of the carbohydrate residue. In the ^{13}C NMR residue the signals of one D-xylose residue were easily traced (Table 2). The values of the chemical shifts of the carbon atoms of the D-xylose residue confirmed the conclusion about the configuration of the anomeric center and the conformation and size of the oxide ring of the monosaccharide residue [16].

A comparative analysis of the ^{13}C NMR spectrum of cycloalpigenin D and cycloalpioside D unambiguously determined the position of the D-xylose residue at C-3.

Thus, cycloalpioside D is 20R,24S-epoxycycloartane-3β,7β,16β,25-tetraol 3-O-β-D-xylopyranoside.

EXPERIMENTAL

For general observations, see [15 and 17]. The following solvent systems were used: 1) chloroform–methanol (15:1); 2) chloroform–methanol–water (70:12:1); 3) chloroform–methanol–water (70:23:4); 4) n-butanol–pyridine–water (6:4:3); and 5) benzene–ethyl acetate (2:1).

The ^1H NMR and ^{13}C NMR spectra were taken on Varian XL-200 and Tesla BS-567 A spectrometers. The PMR spectra were obtained in deuteropyridine or deuterochloroform (δ, ppm, 0–HMDS), and the ^{13}C NMR spectra in deuteropyridine (δ, ppm, 0–TMS).

The circular dichroism curves were measured on a Jasco J-20 spectropolarimeter.

Isolation and Separation of the Triterpenoids of Astragalus alopecurus. The air-dry comminuted epigeal part (14.5 kg) of foxtail milk vetch collected in June, 1987, in the environs of the village of Merke, Dzhambul province, KazSSR, was exhaustively extracted with methanol (120 liters). The methanolic extract, which showed on TLC more than eight products of terpenoid nature, was evaporated to a volume of 3 liters and filtered. The pasty mass remaining on the filter did not contain the desired substances. The filtrate was evaporated to a volume of 1 liter and was diluted with 1 liter of water. The aqueous methanolic solution was then treated with ethyl acetate and with n-butanol.

The ethyl acetate and butanolic extracts were evaporated separately and the residues were dried, giving 257 g of ethyl-acetate-soluble material and 140 gof butanol-soluble material. The ethyl-acetate-soluble material contained all the products detected in the original methanolic extract. The butanolic extract, however, consisted of a highly purified combination of three polar compounds 6–8. Chromatography of the butanol-suluble material (15 g) on a column of silica gel in system 2 and rechromatography of the intermediate fractions led to the isolation of 3 g of substance 6, 2.7 g of substance 7, and 6 g of substance 8.

The ethyl-acetate-extracted material (257 g) was also chromatographed on a column of silica gel with elution successively by chloroform and systems 1-3. On elution of the column with chloroform and system 1, fractions accumulated which contained the weakly polar compounds 1–5. The repeated rechromatography of these fractions on a column in system 1 led to the isolation of 60 mg of substance (I) (0.00041%; here and below the yield is calculated on the air-dry raw material), 70 mg of substance 2 (0.00048%), 50 mg of substance (0.00034%), 167 mg of substance 4 (0.0012%), and 952 mg of substance 5 (0.0065%).

Further washing of the columns with systems 2 and 3 led to a purified mixture of substances 6–8 (69.2 g). The rechromatography of the mixture (10 g) on a column in system 2 gave 3 g of substance 6 (0.336%; the yield here and below is given with allowance for the yield from the butanol-extracted fraction), 4 g of substance 7 (0.3646%), and 1.5 g of substance 8 (0.4577%).

Cycloalpigenin D (I) – substance 4, $C_{30}H_{50}O_5$, mp 209-211°C (from methanol), $[\alpha]_D^{23}$ +46.7 ± 2° (c 1.07; methanol). ν_{max}^{KBr}, cm^{-1}: 3560-3200 (OH); 3040 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 490 (1.8), 475(2.5), 472(4.5), 457(2.5), 454(3.8), 439(3.9), 436(1.6), 431(3.6), 421(2.3), 413(8.9), 395(11.1), 377(4.8), 289(7.5), 271(6.6), 187(7.6), 185(7.6), 173(12.1), 143(100), 125(30.4).

Cycloalpioside D (V) – substance 8, $C_{35}H_{58}O_9$, mp 300-301°C (from methanol), $[\alpha]_D^{26}$ −18.3 ± 2° (c 0.87; methanol). ν_{max}^{KBr}, cm^{-1}: 3500-3250 (OH); 3035 (CH_2 of a cyclopropane ring). PMR spectrum (C_5D_5N), ppm: 0.13 and 0.63 (2 H-19, d, ^2J = 4 Hz; 0.93, 0.99, 1.18, 1.20, 1.20, 1.39, 1.45 (7 × CH_3, s); 4.71 (anomeric proton of D-xylose, d, ^3J = 7 Hz); 4.95 (H-16, m).

Smith Degradation of Cycloalpioside D (V). Cycloalpioside D (920 mg) in 50 ml of methanol was treated with 2 g of sodium periodate in 10 ml of methanol, and the mixture was stirred at room temperature for 2 h. To decompose the excess of oxidant, 1 ml of ethylene glycol was added to the mixture and it was diluted with 100 ml of water. The reaction products were extracted with chloroform. The residue after the usual workup and evaporation of the chloroform extract was dissolved in 50 ml of methanol. This solution was treated with 1 g of sodium tetrahydroborate in small portions, and the resulting reaction mixture was left at room temperature for 1 h. Then it was acidified with 2 ml of concentrated sulfuric acid and was left for 12 h. This 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 1. This led to the isolation of 645 mg of genin (I) with mp 210-211°C (from methanol), $[\alpha]_D^{23}$ + 46 ± 2° (c 1.1; methanol), identical with cylcoalpigenin D.

Acid Hydrolysis of Cycloalpioside D (V). Glycoside (V) (300 mg) was hydrolyzed in 60 ml of a 0.25% methanolic solution of sulfuric acid at the boiling point of the solution for 1.5 h. The reaction mixture was diluted with water and the methanol was evaporated off. The precipitate that deposited was filtered off, washed with water, and chromatographed on a column with elution by system 1. This gave 140 mg of cycloalpigenin D (I), mp 209-211°C (from methanol), $[\alpha]_D^{23}$ + 46.5 ± 2° (c 1.0; methanol).

The filtrate was evaporated to a volume of 20 ml and was boiled for 2 h. The solution was neutralized with type ARA-8p anion-exchange resin. The residue after the removal of the resin and evaporation of the aqueous solution was found by PC in system 4 and by GLC [15] to contain D-xylose.

With the aid of GLC [15] in the presence of D-glucose as standard it was shown that cycloalpioside D (V) contained one D-xylose residue.

The 3,7-Diacetate (II) and 3,7,16-Triacetate (III) of Cycloalpigenin D from (I). Genin (I) (200 mg) was acetylated with 1 ml of acetic anhydride in 2 ml of pyridine for 1.5 h. The residue after evaporation of the solvents was chromatographed on a column with elution by system 5. This yielded 8 mg of the triacetate (III), $C_{36}H_{56}O_8$, mp 190-192°C (from methanol), $[\alpha]_D^{23}$ + 75.6 ± 2° (c 0.37; methanol). $[M]_D$ + 465.7°, ν_{max}^{KBr}, cm^{-1}: 3550 (OH), 3040 (CH_2 of a cyclopropane ring), 1730, 1250 (ester groups). Mass spectrum, m/z (%): $(M-15)^+$ 601(2.9), 556(62.9), 496(80), 481(17.1), 437(34.3), 421(11.4), 395(7.1), 377(28.6), 294(7.1), 253(8.6), 185(11.4), 143(100).

Washing the column with the same system led to the isolation of 184 mg of the diacetate (II), $C_{34}H_{54}O_7$, mp 210-212°C (from methanol), $[\alpha]_D^{23}$ + 55.5 ± 2° (c 0.54; methanol). $[M]_D$ + 318.6°. ν_{max}^{KBr}, cm^{-1}: 3500-3380 (OH), 3045 (CH_2 of a cyclopropane ring), 1740; 1250 (ester groups). Mass spectrum, m/z (%): $(M-15)^+$ 559(0.8), 514(24.0), 499(4.0), 481(3.6), 454(20.8), 421(4.8), 395(8.8), 377(5.2), 352(5.2), 294(4.0), 253(7.2), 227(6.4), 201(6.0), 187(5.6), 185(9.2), 143(100), 125(21.2).

3β,7β,25-Trihydroxy-20R,24S-epoxycycloartan-16-one 3,7-Diacetate (IV) from (II). A solution of 57 mg of the diacetate (II) in 50 ml of acetone at −8°C was treated with 0.1 ml of the Jones reagent [8], and the mixture was stirred for 20 min. To decompose the excess of oxidant, 1 ml of methanol was added to the reaction mixture, and it was evaporated to a volume of 20 ml. Then the solution was poured into 30 ml of water and was treated with chloroform. The chloroform extract was washed with water and evaporated. The residue was chromatographed on a column with elution by system 5. This gave 40 mg of product (IV), $C_{34}H_{52}O_7$, mp 135-138°C (from methanol), $[\alpha]_D^{23}$ − 12.7 + 2° (c 0.32; methanol). ν_{max}^{KBr}, cm^{-1}: 3480–3320 (OH), 1745 (C=O at C-16), 1745; 1255 (ester groups). CD, (c 0.1; ethanol) $\Delta\varepsilon$ = −4.06 (305 nm). Mass spectrum, m/z (%): M^+ 572(2.1), 557(24.3), 539(8.6), 513(37.1), 471(12.9), 454(90), 439(10), 429(14.3), 419(15.7), 411(40), 394(100), 379(20), 369(31.4), 351(35.7), 350(35.7), 314(60), 295(14.3), 254(27.1), 253(27.1), 187(14.3), 185(21.4), 143 (64.3), 125(47.1).

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STRUCTURE OF THE STEROID ALKALOID RADPETINE FROM Petilium raddeana

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A new base with the composition $C_{29}H_{45}NO_3$ has been isolated from the plant Petilium raddeana and has been called radpetine. Its structure has been established as 3β-hydroxy-23,28-epoxy-23-ethyl-$\Delta^{22(N)}$-22,26-iminocholestan-y-one- by the x-ray structural method (diffractometer, CuK_α, 1046 reflections, direct method, MLS in the anisotropic approximation, R = 0.118). Radpetine belongs to a new type of steroid alkaloids with a spiro-methyloxirane grouping at C-23 in the azomethine ring F.

From the plant Petilium raddeana we have isolated a new base with the composition $C_{29}H_{45}NO_3$ (M^+ 455 in the high-resolution mass spectrum), which has been called radpetine (I). The structure of (I) has been studied by IR-, PMR-, and mass-spectral methods, and this has enabled it to be assigned to the steroid alkaloids containing one ketone and one hydroxy group. However, because of the small amount of substance isolated and the unusual spectral characteristics of the nitrogen-containing part of the molecule of (I) it was impossible to establish its structure completely. In order to determine the structure and stereochemistry of radpetine unambiguously we have made an x-ray structural investigation of its hydrochloride.

*Deceased.

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