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STEROLS AND STEROL GLYCOSIDES OF Bryonia alba

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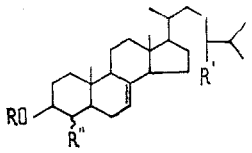
The roots of Byronia alba have long been widely used in the folk medicine of many countries. In view of this, we are systematically studying the chemical composition of extracts of the roots of this plant [1].

The present paper describes the identification of the least polar glycosidic fraction J (TLC, reagents a, b, and d), and also of fractions of free sterols S not differing in their chromatographic mobilities and the red coloration of the spot on TLC (reagent d) from the aglycones of the glycosides J.

The compositions and amounts of the phytosterols and their glycosides in fractions S and J are as follows:



				Amount, %	Fraction
I	R=D-glucopyranosyl,	R'=H, R"=H		1	J
II	"	Me	"	4	
III	"	Et	"	40	
IV	"	=CH_2	"	7	
V	"	=$CHCH_3$	"	42	
VI	"	Et	Me	2	
VII	"	=$CHCH_3$	"	4	
VIII	R = H	H	H	1	S
IX	"	Me	"	5	
X	"	Et	"	46	
XI	"	=CH_2	"	3	
XII	"	=$CHCH_3$	"	42	
XIII	"	Et	Me	2	
XIV	"	=$CHCH_3$	"	1	

Glycoside (I), detected on TLC in the form of a homogeneous spot, was isolated by column chromatography of a chloroform extract on silica gel, followed by recrystallization, in the form of white crystals melting at 211-213°C.

As early as 1911, Power and Moore [2] in a study of the composition of the roots of Bryonia isolated a substance with the same melting point which they named "bryonol." For it they established the empirical formula $C_{22}H_{36}O_4$, but the structure remained unknown. Later, Klein put forward the hypothesis that "bryonol" was actually a "glycoside of the phytosterol group" [3].

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TABLE 1. Main Ions Formed in the Mass-Spectrometric Fragmentation of the Sterols of Bryonia alba and their Derivatives*

Ion	R	H†						H†	Me‡						
	R'	H	Me	Et	=CH_2	=$CHCH_3$	Et	=$CHCH_3$	H	Me	Et	=CH_2	=$CHCH_3$	Et	=$CHCH_3$
	R''	H	H	H	H	H	Me	Me	H	H	H	H	H	Me	Me
M M^+		386 (80)	400 (80)	414 (80)	398 (20)	412 (20)	428 (80)	426 (20)	400 (36)	414 (34)	428 (35)	412 (25)	426 (20)	442 (38)	440 (180)
a M—Me		371	385	399	383	397	413	411	385 (6)	399 (6)	413 (7)	397 (5)	411 (7)	427 (7)	425 (5)
b M—ROH		368	382	396	380	394	410	408	368 (2)	382 (2)	396 (3)	380 (3)	391 (3)	410 (3)	408 (3)
c M—Me—ROH		353	367	381	365	379	395	393	853 (4)	367 (4)	381 (5)	365 (4)	379 (8)	395 (4)	393 (3)
d M—side chain (s.c.)		273	273	273	273	273	287	287	287 (35)	287 (34)	287 (36)	287 (14)	287 (15)	301 (33)	301 (17)
e M—s.c. —ROH		225 (100)	225 (100)	225 (100)	225 (50)	225 (50)	269 (100)	269 (50)	255 (25)	255 (25)	255 (24)	255 (15)	255 (16)	269 (24)	269 (16)
f M—s.c. —27		246	246	246	246	246	260	260	260 (3)	260 (2)	260 (2)	260 (3)	260 (1)	274 (3)	274 (4)
g M—s.c. —27—Me		231	231	231	231	231	245	245	245 (4)	245 (1)	245 (4)	245 (3)	245 (1)	259 (4)	259 (3)
h M—s.c. —27—Me—ROH		213	213	213	213	213	227	227	213 (15)	213 (15)	213 (16)	213 (7)	213 (8)	227 (13)	227 (7)
i M—s.c. —27—RO		229	229	229	229	229	243	243	229 (12)	229 (13)	229 (13)	229 (9)	229 (8)	243 (13)	243 (7)
j M—(C_{23}—C_{27})—H					314 (80)	314 (80)		328 (80)				328 (7)	328 (8)		342 (7)
k M—(C_{23}—C_{27})—H—ROH					296	296		310				296 (1)	296 (1)		310 (1)
l j—43					271 (100)	271 (100)		285 (100)				285 (18)	285 (17)		299 (17)
m j—43—ROH					253	253		267				253 (8)	253 (8)		267 (8)
n M—(C_{23}—C_{27})—Me—H					299	299		213				313 (6)	313 (6)		327 (5)
o M—(C_{23}—C_{27})—Me—H—ROH					281	281		295				281 (4)	281 (4)		295 (4)
p M—s.c. —27—Me—2H—ROH					211	211		225				211 (5)	211 (6)		225 (5)

TABLE 1 (continued)

Ion	R	TMS						TMS	Ac						
	R'	H	Me	Et	=CH_2	=$CHCH_3$	Et	=$CHCH_3$	H	Me	Et	=CH_2	=$CH\ CH_3$	Et	=$CHCH_3$
	R''	H	H	H	H	H	Me	Me	H	H	H	H	H	Me	Me
M M^+		458 (65)	472 (60)	486 (63)	470 (24)	484 (8)	500 (60)	498 (10)	428 (75)	442 (72)	456 (70)	440 (12)	454 (14)	470 (66)	468 (5)
a M—Me		443 (15)	457 (13)	471 (14)	455 (25)	469 (10)	485 (12)	483 (10)	413 (20)	427 (21)	441 (20)	425 (8)	439 (10)	455 (18)	453 (3)
b M—ROH		368 (10)	382 (11)	396 (10)	380 (12)	394 (3)	482 (8)	480 (2)	368 (5)	382 (4)	396 (5)	380 (4)	394 (4)	410 (7)	408 (2)
c M—Me—ROH		353 (15)	367 (15)	381 (14)	365 (15)	379 (6)	467 (20)	465 (3)	353 (13)	367 (12)	381 (14)	365 (6)	379 (6)	395 (13)	393 (3)
d M side chain (s.c.)		345 (5)	345 (5)	345 (4)	345 (22)	345 (8)	359 (3)	359 (2)	315 (10)	315 (10)	315 (11)	315 (3)	315 (2)	329 (10)	329 (3)
e M—s.c. —ROH		255 (100)	255 (100)	255 (100)	255 (47)	255 (18)	269 (100)	269 (20)	255 (100)	255 (100)	255 (100)	255 (50)	255 (45)	269 (100)	269 (15)
f M—s.c. 27		318 (3)	318 (3)	318 (5)	318 (5)	318 (8)	332 (2)	332 (3)	288 (6)	288 (5)	288 (5)	288 (6)	288 (6)	302 (5)	302 (5)
g M—s.c. —27—Me		303 (5)	303 (4)	303 (3)	303	303	317 (9)	317	273 (15)	273 (17)	273 (16)	273 (10)	273 (10)	287 (15)	287 (3)
h M—s.c. —27—Me—ROH		213 (40)	213 (41)	213 (40)	213 (40)	213 (40)	227 (45)	227 (22)	213 (51)	213 (50)	213 (52)	213 (28)	213 (25)	227 (48)	227 (15)
i M—s.c. —27—RO		229 (30)	229 (32)	229 (25)	229 (22)	229 (12)	243 (32)	243 (15)	229 (33)	229 (30)	229 (32)	229 (12)	229 (13)	243 (28)	243 (5)
j M—(C_{23}—C_{27})—H					386 (45)	386 (63)						356 (50)	356 (48)		370 (50)
k M—(C_{23}—C_{27})—H—ROH					296 (10)	296 (14)		400 (20)				296 (5)	296 (5)		310 (5)
l j—43					343 (100)	343 (100)		310 (3)				313 (100)	313 (100)		327 (100)
m j—43—ROH					253 (25)	253 (14)		357 (100)				253 (7)	253 (6)		267 (10)
n M—(C_{23}—C_{27})—Me—H					371 (6)	371 (5)		267 (7)				341	341		355
o M—(C_{23}—C_{27})—Me—H—ROH					281 (17)	281 (20)		385 (5)				281 (2)	281 (3)		295
p M—s.c. —27—Me—2H—ROH					211 (12)	211 (10)		295 (19)				211	211		225 (2)
								225 (10)							

*The m/e values of the ions are shown, the relative intensities of the corresponding peaks being given in parentheses.

†Since no satisfactory GL separation was achieved for the free alcohols, the approximate values of the intensities of the strongest peaks are given in parentheses.

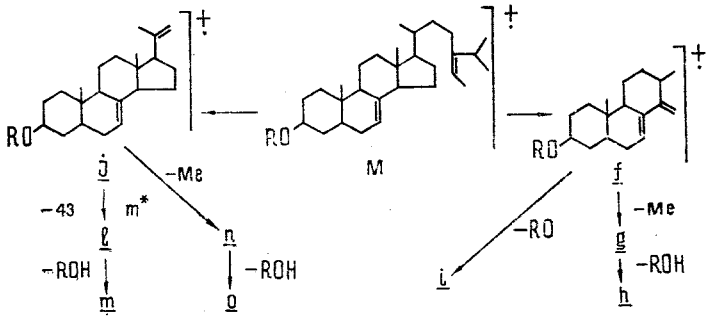
‡Maximum peak at m/e 43.

The acid hydrolysis of the glycosidic fraction J formed glucose and a mixture of sterols giving a homogeneous spot on TLC in various solvent systems. The sterols were identified mainly by chromato-mass-spectrometric analysis of the aglycones [4, 5], their acetates [4, 5], and their methyl and trimethylsilyl ethers [4, 5] (Table 1).

Characteristic for the mass spectra of all the derivatives of Δ^7-sterols are the peaks of ions d, f, g, and i. The high itensity of the peaks of the molecular ions and the maximum intensity of the peak of ion e for the monoenes also distinguishes the mass spectra of the Δ^7-sterols and their derivatives from the mass spectra of the Δ^5-sterols. The absence of the peak of the $[M - 129]^+$ ion in the mass spectra of the TMS derivatives enables us to exclude the possibility of the presence of a Δ^5-bond [5].

In the mass spectra of the diunsaturated sterols and their derivatives, the strongest peaks are those of ions j and l, which shows the C-24–C-28 position of the second double bond [4, 5].

The mass-spectrometric fragmentation of the methyl ethers of sterols (VIII-XIV) has not been studied previously. The main routes of the fragmentation of the molecular ions of the latter obey the same laws as for the sterols themselves, their acetates, and their TMS ethers [4, 5] (Scheme 1).



Scheme 1

The strongest peaks in the mass spectra of the methyl ethers are those of the ions e, d, h, and i, formed by the detachment of the side chain. When there is a double bond in the side chain, the ions j-p are also formed, but the intensities of their peaks are comparatively low. The Δ^7 position of the double bond, and, in addition to this, the trans-syn-trans-syn-trans configuration of rings A, B, and C were confirmed by the Fieser test [6].

The deduction of the β configuration of the hydroxyl at C-3 was made on the basis of the PMR spectra of the aglycone (broadened multiplet of the geminal hydrogen atom at δ 3.2-3.6 ppm) and of its acetate (δ 4.4-4.8 ppm).

The quantitative ratio of the aglycone and of the glucose residue (1 : 1) was shown by the GLC of the trimethylsilyl ethers of the methyl glucoside formed by the acid methanolysis of the glycosidic fraction J.

The presence of the signals of a proton geminal to the glycosidic oxygen atom at δ 4.57 ppm with $J = 7.5$ Hz in the PMR spectrum of the tetraacetate of (I) shows the β configuration of the glycosidic bond [7]. It must be observed that glycosides of fraction J (I-VII) are close in structure to daucosterol (eleutheroside A) isolated from ginseng [8], acanthopanax [9], eleutherococcus [10], and Polygonum coriarium [11].

The phytosterol fraction S (VIII-XIV) was isolated by column chromatography on silica gel and appeared on TLC in various solvent systems in the form of a homogeneous spot. The UV spectrum of fraction S showed the absorption maxima of an α,β-unsaturated γ-lactone, which is due to the presence of minor amounts of such a compound. The further purification of fraction S from the lactone was performed by alkaline hydrolysis of the fraction and preparative TLC of the components of the reaction mixture. After recrystallization of fraction S isolated in this way, white crystals melting at 123-127°C were obtained.

Chromato-mass-spectrometric analysis (see above and Table 1) showed that the qualitative composition of fraction S was similar to that of the aglycones of the glycosidic fraction J, but the amounts of the various components showed slight differences.

The possibility of the formation of fraction S in the drying of the plant by the hydrolytic cleavage of fraction J by a glycosidase present in the plant tissue must be excluded, since fraction S was also found to be present in an extract of fresh roots treated with hot isopropanol.

EXPERIMENTAL

Material and General Methods. For column and thin-layer chromatography we used type KSK silica gel, 80-100 and 250-300 mesh, respectively. In TLC we used the following solvent systems: 1) $CHCl_3$–MeOH–H_2O (65 : 25 : 4); 2) benzene–MeOH (11 : 2); 3) $CHCl_3$–MeOH (9 : 1); 4) $CHCl_3$–benzene–EtOAc (3 : 2 : 1); 5) $CHCl_3$–MeOH–AcOH–H_2O (80 : 13 : 8 : 0.3); 6) $CHCl_3$–MeOH–AcOH–H_2O (90 : 8 : 1 : 0.8); 7) benzene–ether–EtOH–AcOH (80 : 2 : 1 : 0.2); and 8) hexane–ether–AcOH (80 : 20 : 1).

To detect the substances on the chromatograms, the plates were sprayed with: a) 50% H_2SO_4 followed by heating to 180°C; b) a 0.5% solution of α-naphthol [12], c) a 0.2% solution of anthrone in H_2SO_4, d) a 1% aqueous ethanolic (1 : 1) solution of vanillin in 15% H_3PO_4, and e) a 0.01% solution of morin followed by observation in UV light.

PC was performed on "Leningrad" paper from the Volodarskii mill by the descending method in the following solvent systems: 9) n-BuOH–AcOH–H_2O (4 : 1 : 5, upper layer); 10) n-BuOH–pyridine–benzene–H_2O (5 : 3 : 1 : 3); and 11) water-saturated phenol. The spots were revealed with aniline phthalate.

The trimethylsilyl ethers of the methyl glycosides and phytosterols, and also the methyl ethers and acetates of the latter were analyzed on a "Chrom-4" chromatograph fitted with a flame-ionization detector. For separation we used a column (1000 × 4 mm) with 2% of E-301 silicone on silanized Chromaton N-AW-HMDS.

The GLC of the phytosterols and their derivatives was carried out at 250°C and that of the methylsilyl ethers of the methyl glycosides at temperatures of 150 → 220°C (4°C/min). The carrier gas was helium 30-50 ml/min).

Combined GLC–mass spectrometry was performed on a LKB-9000 instrument with an energy of the ionizing electrons of 70 eV. In all cases we used the column mentioned above and the same conditions of chromatography.

The IR spectra were recorded on a UR-20 spectrophotometer, the UV spectra on a Specord UV-Vis spectrophotometer in EtOH (c 0.01 mg/ml), and the PMR spectra on a Varian 60-A spectrometer at 60 MHz in CCl_4 and $CDCl_3$ with Me_4Si as internal standard.

Isolation of the Glycoside Fraction J and the Sterol Fraction S. The dried and comminuted roots of B. alba (16.1 g) were extracted with $CHCl_3$ (3 × 0.5 liter). The combined extract was evaporated in vacuum. The residue (2.2 g) was deposited on a column (100 × 2.5 cm) containing 150 g of silica gel. The substances were eluted from the column with mixtures of petroleum ether and ether – (98 : 2) (590 ml), 85 : 15) (700 ml), (1 : 1) (300 ml) – with ether (450 ml), with $CHCl_3$ (1020 ml), with $CHCl_3$–Me_2CO (1 : 1) (1440 ml), and with Me_2CO (1500 ml). The fractions (20 ml each) eluted by the $CHCl_3$–Me_2CO (1 : 1) mixture, which contained the glycoside (I) were combined, and the solvent was evaporated off. The residue (195 mg) was recrystallized from benzene and three times from a mixture of $CHCl_3$ and MeOH and from MeOH. This gave white crystals of the glycosidic fraction J mp 211-213°C, R_f 0.75 (system 1, revealing agents a-d), 0.60 (system 5; a-d), $[\alpha]_D^{20}$ −23.2 ± 0.5°.

ν_{max}^{KBr} 3400, 2960, 2940, 2880, 2860, 1645, 1465, 1445, 1380, 1365, 1045 cm^{-1}.

The fractions eluted with ether and containing the free sterols S were combined, and the solvent was evaporated off. The residue (218 mg) was dissolved in 10 ml of benzene, the benzene layer was separated from the insoluble residue, the solvent was evaporated, and the residue was repeatedly recrystallized from MeOH. This gave white crystals with mp 108-110°C, R_f 0.62 (system 6; a, d); 0.86 (system 1, a, d). λ_{max}^{EtOH} 208 (log 4.28), 2.23 (log 3.33), 280 (log 2.52) nm, $\nu_{max}^{CCl_4}$ 3630, 2976, 2950, 2880, 2865, 1740, 1645, 1380, 1365 cm^{-1}. A mixture of 60 mg of the crystals (mp 108-110°C) and 3 ml of 0.25 N KOH in EtOH was boiled for 1.5 h and, after cooling, it was diluted with 5 ml of H_2O, acidified with 5% HCl, and extracted with ether (3 × 10 ml). The combined ethereal extract was washed with 3 ml of H_2O and was dried with sodium sulfate, the solvent was evaporated off, and the residue was subjected to preparative TLC in system 4 (revealing agent e). This gave 43 mg of crystals with mp 123-127°C (MeOH), R_f 0.62 (system 6; a, d); 0.86 (1; a, d); 0.83 (2; a, d), ν_{max}^{KBr} 3400, 2960, 2940, 2880, 2860, 1645, 1465, 1445, 1380, 1365 cm^{-1}. The PRM spectrum showed the signals of protons at δ 4.9-5.2 ppm (1.5 H, multiplet, $=C-\underline{H}$) and 3.2-3.6 ppm (1H, multiplet, $\underline{H}-C(OH)-C-$). No selective absorption at 210-300 nm was observed in the UV spectrum.

Acetylation of Fraction S. A mixture of 32.6 mg of fraction S and 3 ml of pyridine–Ac_2O (2 : 1) was kept at 60°C for 2 h, and then the solvent was evaporated off, and the residue was dissolved in 1 ml of $CHCl_3$, deposited on a column (30 × 1 cm) containing 5 g of silica gel, and eluted with 50 ml of $CHCl_3$. This gave 33 mg of the acetate. mp 142-144°C, R_f 0.77 (system 7; a, d); 0.87 (4; a, d); 0.77 (8; a, d). The PMR spectrum showed the signals of protons at δ 4.9-5.3 ppm (1.5 H; multiplet, $=C-\underline{H}$); 4.4-5.8 ppm (1 H, multiplet, $\underline{H}-C(-OAc)-C-$) 1.92 ppm (3 H; singlet, $C\underline{H}_3-C(=O)-O-$).

Methylation of Fraction S. Using the method of Deferrari et al., [13], 6.2 mg of fraction S was methylated with diazomethane in the presence of BF_3 etherate. This gave 6.1 mg of methyl ethers with R_f 0.75 (system 4; a, d); 0.68 (6; a, d).

Trimethylsilyl Ethers of S. Using the method of Brobst and Lott [14], 2.8 mg of fraction S was silylated with HMDS–CF_3COOH–pyridine (9 : 1 : 10).

Acetylation of the Glycoside Fraction J. Glycoside fraction J (15.2 mg) was acetylated in a similar manner to S (80°C, 6 h). This gave 15.6 mg of acetates with mp 145-147°C (MeOH), R_f 0.81 (system 3; a, d); 0.62 (7; a, d); 0.64 (4; a, d); 0.77 (2; a, d).

The PMR spectrum showed the signals of protons at δ 1.9-2.1 ppm (12 H, multiplet, $C\underline{H}_3-C(=O)-O-$) 4.57 (1 H, doublet, J = 7.5 Hz).

Hydrolysis of Glycoside Fraction J. A mixture of 5 mg of glycoside fraction J and 1 ml of 1 N HCl was boiled for 6 h. After cooling, the reaction mixture was washed with $CHCl_3$ (2 × 2 ml), and glucose was identified in the aqueous layer by PC in systems 9-11.

Methanolysis of Glycoside Fraction J. A mixture of 18.8 mg of the glycoside fraction J and 3 ml of 2.5% HCl in MeOH was boiled for 22 h. After the mixture had been cooled, it was neutralized with Dowex-1 (OH^-), the resin was filtered off and was washed with 2 ml of MeOH, and the filtrate was diluted with 0.2 ml of H_2O and extracted with hexane (3 × 6 ml). The aqueous methanolic layer was evaporated to dryness, 7.6 mg of mannitol was added to the residue, and it was silylated by the method of Brobst and Lott [14]. The GC analysis of the α and β anomers of the methyl 2,3,4-6-tetra-O-trimethylsilylglucosides obtained in this way (identical with an authentic sample according to R_f values) showed the presence of 5.83 mg of glucose in the initial sample.

The hexane extract contained 12.8 mg of the aglycone (at M_{agl} = 414, the aglycone/glucose ratio = 1). mp 97-99°C (MeOH), R_f 0.62 (system 6; a, d); 0.86 (1; a, d); 0.83 (2; a, d).

The acetates and methyl and trimethylsilyl ethers of the aglycones of the glycoside fraction J were obtained in the same way as for the sterol fraction S.

SUMMARY

It has been shown that the roots of Bryonia alba contain cholest-7-en-3β-ol, 24-methylcholest-7-en-3β-ol, 24-ethylcholest-7-en-3β-ol, 24-methylenecholest-7-en-3β-ol, 24-ethylidenecholest-7-en-3β-ol, 24-ethyl-4-methylcholest-7-en-3β-ol, 24-ethylidene-4-methylcholest-7-en-3β-ol, and also previously undescribed 3-O-β-glucopyranosides of the above-mentioned sterols.

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INFLUENCE OF SOLVENTS ON THE PARAMETERS OF THE NMR SPECTRA OF *Vinca* ALKALOIDS. V

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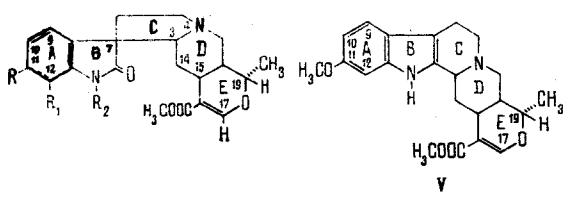
UDC 577.94:543.42:542.61

Continuing a study of the influence of solvents on the parameters of the NMR spectra of alkaloids [1], we give the results for a number of hydroxyindole bases belonging to the allo series (majdine (I), isomajdine (II), and N-acetylvinerine (III), and the epiallo series (vineridine (IV)). In addition, for the purpose of comparing results and checking our conclusions concerning the influence of solvents on the parameters of the PMR spectra of alkaloids of the hydroxyindole series we have studied the indole alkaloid reserpinine (V). The stereochemistry and absolute configurations of bases (I-V) have been established previously [2, 3].



V

I. $R = R_1 = OCH_3$, $R_2 =$ $= H$, 7R, 3S, 4R
II. $R = R_1 = OCH_3$, $R_2 =$ $= H$, 7S, 3S, 4R
III. $R = OCH_3$, $R_1 = H$, $R_2 = Ac$, 7S, 3S, 4R
IV. $R = OCH_3$, $R_1 = R_2 =$ $= H$, 7S, 3R, 4S

Influence of Aromatic Solvents on the Chemical Shifts (CSs) of the Bases (I-IV). As can be seen from Tables 1-4, the CSs of the $C_{19}-CH_3$ protons in benzene for majdine, isomajdine, and N-acetylvinerine shift upfield by +0.18 ppm, and in vineridine by +0.36 ppm. The signal of the H_{19} proton in alkaloids (I-III) undergoes an appreciable paramagnetic shift, while in the base (IV) this signal is shifted upfield. It has been established previously [4] that the difference in the CSs of $C_{19}-CH_3$ and H_{19} in solutions of $CDCl_3$ in the alkaloids of the allo and epiallo series are due mainly to the descreening influence on them of the unshared electron pair (UEP) of the N_4 nitrogen atom. It is known that the benzene molecule, in the main, strives to place itself as far as possible from the negatively-charged part of the molecule [5, 6]. As can be seen from Dreiding stereomodels, in the allo alkaloids the protons at the C_{19} carbon atom are located between the unshared electron pairs of the N_4 and O_{18} atoms and, obviously, the latter prevent the interaction of C_6D_6 with this part of the molecule. In the epiallo bases, the UEP of the N_4 atom is α-oriented and the approach of the molecules of the benzene solvent to the protons at C_{19} is facilitated. In view of this, the values of $\Delta^{C_6D_6}_{CDCl_3}$ for $C_{19}-CH_3$ differ in magnitude while for H_{19} the sign is different. Consequently, differences in the configuration of the N_4 center of the compounds investigated not only cause changes in the CSs of the protons mentioned above but are also the cause of the different influences of benzene on the CSs of these groups.

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