LITERATURE CITED

1. Kh. B. Alloyarov, A. Abdusamatov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 143 (1970).
2. H. Hauth and D. Stauffacher, Helv. Chim. Acta, 47, 185 (1964).
3. W. C. Wildman and D. T. Bailey, J. Am. Chem. Soc., 89, 5514 (1967).
4. W. C. Wildman and D. T. Bailey, J. Org. Chem., 33, 3749 (1968).

ALKALOIDS OF *Korolkovia severtzovii*

STRUCTURE OF KORSILINE

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Continuing an investigation of the alkaloids of the epigeal part of *Korolkovia severtzovii* Rgl., the mother liquor from korseveridine [1] was chromatographed on a column of silica gel. A chloroform eluate yielded a base with mp 238-240°C (acetone), $[\alpha]_D$ +79.9° (c 0.713; ethanol) and the new alkaloid korsiline with mp 194-196°C (acetone), $[\alpha]_D$ ±0 (c 0.8; ethanol), with the composition $C_{27}H_{43}NO_2$ (I). Korsiline forms a digitonide, which shows the presence of a 3β-OH group.

IR spectrum of (I), ν_{max}, cm^{-1}: 3350, 1082 (OH), 2980-2840; 1467 ($-CH_2-$, $-CH_3$), 1715 (C=O), 1663 (C=N), and the "fingerprint" region of the spectrum of (I) differed from that of the steroid alkaloid petiline (II) [2, 3]. The mass spectrum of (I) showed the peaks of ions with m/e 97 (4%), 98 (6%), 110 (8%); 111 (54%), 112 (8.5%); 124 (21%), 125 (100%), 126 (14%), 138 (7%), 139 (3%), 150 (21%), 151 (16%), 152 (8%), 164 (19%), 165 (17%), 166 (5%), 398 (25%), (M–15) (24%), 413 (31%) (M^+), which are characteristic for typical steroid alkaloids [3-5]. With acetic anhydride in pyridine, (I) formed amorphous O,N-diacetylkorsiline (III). IR spectrum of (III), ν_{max}, cm^{-1}: 1733, 1245 (O-acetyl), 1715 (C=O), 1670 ($N-COCH_3$).

Korsiline has the same composition as petiline, and their IR and NMR spectra are similar but not identical. Korsiline differs from petiline in its R_f values, melting point, and specific rotation, and also in the intensities of the peaks of the ions in the mass spectrum. Below we give the characteristics of the NMR spectra of (I-IV) [for (II) and (IV) see [2, 3]; s) singlet; d) doublet; m) multiplet]:

Substance	$19-CH_3$, s	$18-CH_3$, s	$21-CH_3$, d	$27-CH_3$, d	$OCOCH_3$, s	$N-COCH_3$, s	$\underline{CH}-OCOCH_3$, m	Olefinic, m
I	0,68	0,63	0,86 J = 7 Hz	1,03 J = 7,5 Hz	—	—	—	—
II	0.68	0.63	0.83	1,01	—	—	—	—
III	0,70	0,60	0.91 J = 7 Hz	1.04 J = 7 Hz	2,00	2,11	4,60	5.12
IV	0,69	0,57	0.89	1,14	1,95	2,06	4.60	5.10

The results of a comparative study of the chemical shifts of the $19-CH_3$ and $18-CH_3$ protons in the NMR spectra of (I) and (III) with those of (II) and of O,N-diacetylpetiline (IV) [3] showed that (I) and (II) have the same heterocyclic skeleton and the trans linkage of rings A/B, B/C, and C/D; there is a β-oriented hydroxy group at C_3 and a carbonyl oxygen at C_6 [3]. However, in the NMR spectrum of (I), unlike that of (II), the signals from the $21-CH_3$ protons are shifted downfield by 3 Hz and those from the $27-CH_3$ protons by 2 Hz. In the NMR spectrum of (III), the signal from the $27-CH_3$ protons is observed in a stronger field by 10 Hz than those of (IV) [3].

The facts given above show that (I) is a diastereoisomer of (II) with respect to the C_{20} or C_{25} asymmetric center, but the configuration of these centers have not yet been determined for either of these alkaloids.

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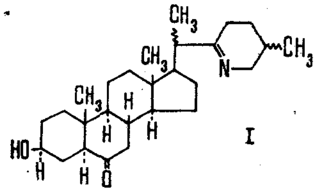
On the basis of the facts given, it may be considered that korsiline has the most probable structure and partial configuration (I):



I

LITERATURE CITED

1. K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 367 (1976).
2. R. N. Nuriddinov, B. Babaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 168 (1968).
3. R. N. Nuriddinov, B. Babaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 604 (1969).
4. G. Adam, K. Schreiber, T. Tomko, and A. Vassova, Tetrahedron, 23, 167 (1967).
5. A. M. Khashimov, R. Shakirov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 339 (1970)

SYNTHESIS OF QUATERNARY SALTS OF DI(PYRROLIZIDIN-4-YLMETHYLDIOXOLANYL)ETHANE AND -ETHYLENE

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Quaternary salts of di(aminomethyldioxolanyl)ethane and -ethylene possess a high curaremimetic activity [1]. With a change in the substituents of the quaternary nitrogen atoms their muscle-relaxing activity is modified. One of the preparations of this series has entered medical practice under the name of "dioksonii." It appeared of interest to synthesize derivatives of di(methyldioxolanyl)ethane or -ethylene with pyrrolizidine nuclei. With this aim, we have studied the reaction of 1,2-di(4-chloromethyl-1,3-dioxolan-2-yl)ethane and -ethylene (I and IV) with pyrrolizidine alkaloids and their derivatives. The initial 1,2-di(4-chloromethyl-1,3-dioxolan-2-yl)ethane and -ethylene were obtained by the reaction of the methyl diacetals of succinaldehyde and malealdehyde with glycerol α-monochlorohydrin [2, 3]. The reaction took place smoothly when one equivalent of 1,2-di(4-chloromethyl-1,3-dioxolan-2-yl)ethane or -ethylene was heated with two equivalents of the base (lindelofine (IIa), lindelofidine (IIb) or hydroxyheliotridane (IIc)) at 135-145°C for 4-5 h; the bisquaternary salts (IIIa-b and Va-c) were formed with high yields (75-90%).

The yields and some physicochemical properties of the compounds obtained are given below (compounds (IIIa and b) and (Va-c) were purified by reprecipitation of ethanolic solutions with ether):

The structures of the compounds obtained were shown by the results of elementary analysis and by IR spectroscopy.

TABLE 1

Compound	Initial compound	Yield, %	mp, °C	Empirical formula
IIIa	I, IIa	91	209—10	$C_{40}H_{70}O_{12}N_2Cl_2$
IIIb	I, IIb	91	170—72	$C_{26}H_{46}O_6N_2Cl_2$
Va	IV, IIa	75	68—70	$C_{40}H_{68}O_{12}N_2Cl_2$
Vb	IV, IIb	84	88—90	$C_{26}H_{44}O_6N_2Cl_2$
Vc	IV, IIc	77	168—70	$C_{26}H_{44}O_6N_2Cl_2$

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