

Compounds (III) and (IV) are formed through an intermediate immonium salt (II) which it is possible to isolate in the individual state. Compound (III) is converted into (IV) even when it is mixed with an aqueous solution of dimethylamine at room temperature.

The structures of the compounds obtained were shown by the results of elementary analysis and by IR, PMR, and mass spectroscopy. The IR spectra of (III) had absorption bands at 1650 cm^{-1} ($\nu\text{C=O}$) and $3350\text{--}3600\text{ cm}^{-1}$ (νOH). The existence of compound (III) in the enolic form was confirmed by a qualitative reaction with ferric chloride. The PMR spectrum (IV) had the signals of the protons of a N-dimethyl group at 2.58 ppm (6 H, singlet), of two methylene groups at 2.60 ppm (2 H, triplet) and 3.90 (2 H, triplet), and of an aromatic ring at 7.02–7.58 ppm (3 H, multiplet) and 8.03 ppm (1 H, doublet). The signals of an olefinic proton appeared in the 7.35-ppm region. The PMR spectrum of (III) contains the signals of the protons of two methylene groups at 2.85 and 3.96 ppm and of an aromatic ring in the 7.15–7.80 and 8.49 ppm regions. The mass spectrum of (III) was characterized by the presence of ions with m/e 214 (M^+) and 185 ($\text{M} - \text{CHO}$), and that of (IV) by an ion with m/e 241 (M^+).

LITERATURE CITED

1. H. H. Bosshard, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1659 (1959); E. Campaigne and W. Archer, *Org. Synth.* (Russian translation), **5**, 22 (1954); R. Silverstein, E. Ryskiewicz, and C. Willard, *Org. Synth.* (Russian translation), **8**, 44 (1958).
2. M. R. Chandramohan and S. Seshadri, *Ind. J. Chem.*, **12**, 940 (1974); S. Seshadri, M. S. Sadessai, and A. M. Betrabet, *Ind. J. Chem.*, **7**, 662 (1969).
3. W. E. Hanford and R. Adams, *J. Amer. Chem. Soc.*, 921 (1935).
4. Kh. M. Shakhidoyatov, A. Irisbaev, E. Oripov, and Ch. Sh. Kadyrov, *Khim. Prirodn. Soedin.*, 557 (1976).

EPIMACRONINE FROM *Ungermia spiralis*

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We have studied the bulbs of *Ungermia spiralis* gathered on May 25, 1974, in the Kara-Kala region of the Turkmen SSR. They have not been investigated previously.

The alkaloids were extracted by the usual method. From the mixture of bases were isolated lycorine (0.36% of the weight of the dry plant), tazettine, hippeastrine [1], and a new base (I).

Alkaloid (I) had mp $104\text{--}105^\circ\text{C}$, composition $\text{C}_{18}\text{H}_{19}\text{NO}_5$, M^+ 329, $[\alpha]_D^{+109}$ (c 0.72; chloroform), R_f 0.74 in the benzene-methanol (4:1) system in a thin layer of silica gel. UV spectrum of (I), λ_{max} , nm: 232, 272, 312 ($\log \epsilon$ 4.67, 3.99, 3.94). IR spectrum of (I), λ_{max} , cm^{-1} : 1715 ($>\text{C=O}$), 162 ($>\text{C=C}<$), 1500, 1480, 1440 (aromatic ring).

The NMR spectrum of (I) (CDCl_3 , JNM-4H-100 MHz instrument, HMDS, τ scale) had the following signals (ppm): singlets at 2.49 and 3.17 (aromatic protons at C_9 and C_{12}), 4.02 (2 H, $-\text{O}-\text{CH}_2\text{O}$), 6.60 (3H, $-\text{OCH}_3$), and 7.53 (3 H, $>\text{N}-\text{CH}_3$), and one-proton doublets from two olefinic protons at 3.8 and 4.67 ($J = 11\text{ Hz}$) for the protons at C_2 and C_1 , respectively.

A comparison of the characteristics given with those of macronine [2] and of synthetic epimacronine [3, 4] shows that (I) is epimacronine and this is the first time that it has been isolated from plants.

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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), $[\alpha]_D^{+79.9^\circ}$ (c 0.713; ethanol) and the new alkaloid korsiline with mp 194-196°C (acetone), $[\alpha]_D \pm 0$ (c 0.8; ethanol), with the composition $C_{27}H_{43}NO_2$ (I). Korsiline forms a digitonide, which shows the presence of a 3 β -OH group.

IR spectrum of (I), ν_{\max} , cm^{-1} : 3350, 1082 (OH), 2980-2840; 1467 ($-\text{CH}_2-$, $-\text{CH}_3$), 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-COCH₃).

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	CH-OCOCH ₃ , m	Olefinic, m
I	0.68	0.63	0.86 J=7Hz	1.03 J=7.5Hz	—	—	—	—
II	0.68	0.63	0.83	1.01	—	—	—	—
III	0.70	0.60	0.91 J=7Hz	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-CH₃ and 18-CH₃ 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 C₃ and a carbonyl oxygen at C₆ [3]. However, in the NMR spectrum of (I), unlike that of (II), the signals from the 21-CH₃ protons are shifted downfield by 3 Hz and those from the 27-CH₃ protons by 2 Hz. In the NMR spectrum of (III), the signal from the 27-CH₃ 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 C₂₀ or C₂₅ asymmetric center, but the configuration of these centers have not yet been determined for either of these alkaloids.

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