versions have been studied by supplying the plants with the tritium-labelled alkaloids [^{3}H] sophocarpine, [^{3}H] matrine, and [^{3}H] pachycarpine.

LITERATURE CITED

1. Yu. K. Kushmuradov, Kh. A. Aslanov, and S. Kuchkarov, Khim. Prirodn. Soedin., 377 (1975).
2. S. Yu. Yunusov, Khim. Prirodn. Soedin., 104 (1966).
3. H. R. Schütte, H. A. Aslanov, and C. Schäfer, Arch. Pharm., 295, 34 (1962).
4. S. Shibata and U. Sankawa, Chem. Ind. (London) 1161 (1963).
5. B. A. Abdusalamov, A. A. Takanaev, Kh. A. Aslanov, and A. S. Sadykov, Uzb. Biol. Zh., 13, No. 2, 10 (1969).
6. H. R. Schütte and D. Knöfel, Z. Pflanzen-physiol, 58, 80 (1968).
7. H. R. Schütte and H. Hindorf, Z. Naturforsch., 19, 855 (1964).
8. H. R. Schütte, H. Hindorf, K. Mothes, and G. Hübner, Ann. Chem., 680, 93 (1964).
9. H. R. Schutte, Angew Chem., 77, 1039 (1965).
10. H. R. Schütte, A. Unverrieht, J. Lehfeld, N. Eberle, and U. Fischer, Z. Chem., 2, 336 (1962).

ALKALOIDS OF *Korolkovia severtzovii*

STRUCTURE OF KORSIDINE

K. Samikov, R. Shakirov,
D. N. Safaeva, and S. Yu. Yunusov

UDC 547.944/945

We have continued our investigation of the alkaloids of *Korolkovia severtsovii* Rgl. [1] growing in Khamzaabade, Fergana oblast. From the epigeal part collected in the flowering stage, by chloroform extraction we isolated 0.93% of combined alkaloids, and from the hypogeal part 1.64%. Separation of the combined alkaloids from the epigeal part gave sevkorine, korseveriline, and severtzidine [2-4], and the new alkaloid korsidine with mp 316-318°C $[\alpha]_D$ ±0°, $C_{27}H_{43}NO_2$ (I).

The IR spectrum of the base showed absorption bands at (cm^{-1}) 3400-3200 (OH), 2975-2830 ($-CH_3$, $-CH_2-$), and 2776 (trans-quinolizidine). The mass spectrum of (I) showed the peaks of ions with m/e 97, 98, 111, 112, 122, 149, 165, 179, 183, 201, 202, 244, (M–29), (M–18), (M–15), 413 (100%) M^+, which are characteristic for C-nor-D-homosteroid alkaloids of the cevine group [5, 6]. The NMR spectrum of korsidine was not recorded because of its poor solubility in organic solvents.

In korsidine, the oxygen atoms are present in the form of secondary hydroxy groups, as was confirmed by the preparation of diacetylkorsidine (II). The IR spectrum of (II) has absorption frequencies at 1738, 1250, and 1232 cm^{-1} (ester C=O).

No signal from an olefinic proton was observed in the NMR spectrum, but in a weak sulfuric acid solution korsidine instantaneously decolorizes potassium permanganate solution, which shows the presence of a double bond.

The oxidation of korsidine with chromium trioxide gave a diketone – korsidinedione (III). In the UV spectrum the latter has λ_{max} 300 nm (log ε 2.39), which is characteristic for unconjugated carbonyl groups. The IR spectrum of (III) had absorption bands at 1710 cm^{-1} (carbonyl in a six-membered ring) and lacked absorption bands of hydroxy groups.

The catalytic hydrogenation of korsidine according to Adams formed dihydrokorsidine (IV). In the IR spectrum of (IV), the fingerprint region was similar to that of petilinine

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.

Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 780-783, November-December, 1976. Original article submitted May 18, 1976.

[7]. Acetylation of dihydrokorsidine with acetic anhydride in pyridine gave diacetyldihydrokorsidine (V). The oxidation of (IV) with chromium trioxide gave dihydrokorsidinedione with mp 226-228°C (VI), identical with petilininedione obtained by the oxidation of petilinine [7] (by melting point and IR, NMR, and mass spectra).

Details of the NMR spectra of (II-VI) are given below (δ, ppm):

Substance	19—CH_3, s	21—CH_3, d	27—CH_3, d	—$OCOCH_3$, s	—$OCOCH_3$, s	CH—$OCOCH_3$, m	CH—$OCOCH_3$, m
II	0.98	0.80	0.80	1.99	1.99	5.05	4.90
III	0.95	0.81	0.81				
IV	0.93	0.80	0.80				
V	0.94	0.81	0.81	1.98	2.00	5.06	4.89
VI	0.87	0.81	0.81				

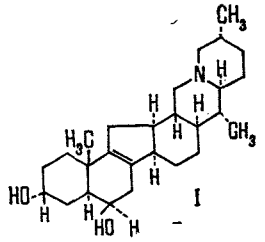
Note. s – singlet; d – doublet; m – multiplet.

The identity of dihydrokorsidinedione with petilininedione confirms the fact that korsidine has the heterocyclic skeleton of cevanine and that the two secondary hydroxy groups are present at positions C_3 and C_6 [7]. Consequently, korsidine differs from petilinine by the presence of a double bond and by the configurations of the hydroxy groups, and the linkage of rings A/B, B/C, C/D, D/E, and E/F in dihydrokorsidine is the same as in petilinine and the 21-CH_3 and 27-CH_3 groups are oriented equatorially in the α positions [7-9].

In the NMR spectra of (II) and (V), multiplets from protons geminal to acetoxy groups at 5.05 and 4.90 ppm show that the acetoxy group at C_3 has the α- and at C_6 the β-axial orientation and, correspondingly, the hydroxy groups at C_3 and C_6 in korsinidine are oriented similarly to the acetoxy groups [10-12].

The upfield displacement of the chemical shifts of the protons of the 19-CH_3 group in (V) and (VI) by 4 and 7 Hz, respectively, in comparison with the NMR spectra of (II) and (III) shows that the double bond in korsidine is present between carbon atoms C_8 and C_9 [11] and excludes other possible positions.

Thus, korsidine has the most probable structure and configuration of 3α,6β-dihydroxy-Δ^8-cevacene (I):



I

EXPERIMENTAL

The homogeneity of the substances was checked by chromatography in a thin layer of alumina in the ethyl acetate–petroleum ether–methanol (5:5:1) system. The revealing agent was Dragendorff's solution.

The UV spectra were taken on a Hitachi spectrophotometer, the IR spectra (KBr) on a UR-20 spectrophotometer, and the NMR spectra on a JNM-4H-100/100 MHz instrument in deuterochloroform [(IV) in $CDCl_3$ + CD_3OD)] with HMDS as internal standard (the values are given in the δ scale), and the mass spectra on an MKh-1303 instrument fitted with a glass system for direct introduction into the ion source.

Isolation and Separation of the Total Alkaloids. The dried comminuted epigeal part of *K. severtzovii* collected on May 23, 1975 in the flowering stage at Khamzaabade, Fergana oblast, (45 kg) was wetted with a 10% solution of ammonia and extracted exhaustively with chloroform. The alkaloids were extracted from the chloroform solution with 10% sulfuric acid. The sulfuric acid solution was made alkaline with ammonia and the mixture of bases was extracted with ether (265.8 g) and chloroform (143 g). In the isolation of the chloroform-soluble alkaloids, 11 g of crystals precipitated with mp 236-238°C (methanol), which proved to be sevkorine.

The total yield of combined alkaloids was 419.8 g (0.93% of the weight of the dried plant).

Korsidine. The combined ether-soluble alkaloids (265.8 g) were treated with acetone, which led to the precipitation of 34.6 g of a mixture of crystals. Treatment of this mixture with methanol yielded 2.5 g of korsidine with mp 316-318°C (methanol), $[\alpha]_D$ ±0° (c 0.89; 10% acetic acid), R_f 0.74, $C_{27}H_{43}NO_2$, M 413 (mass-spectrometrically).

Korseveriline and Severtzidine. The acetone-soluble fraction of the combined alkaloids after the separation of the mixture of crystals (3.2 g) was dissolved in chloroform and separated according to basic strength into 13 fractions by extraction with 3 ml portions of 1% sulfuric acid. The first fraction (1.48 g) was chromatographed on a column of alumina (activity grade II) with elution by chloroform–methanol (10:0.5) collected in 10-15 ml portions. The first eluate yielded korseveriline with mp 240-242°C (methanol) and the subsequent fractions severtzidine with mp 244-245°C (acetone).

Diacetylkorsidine. A mixture of 0.1 g of korsidine, 1 ml of pyridine, and 1.5 ml of acetic anhydride was left at room temperature for 3 days. Then it was evaporated in vacuum and the residue was dissolved in 5% sulfuric acid. The acid solution was made alkaline with ammonia, and the reaction product was extracted with chloroform. This gave amorphous diacetylkorsidine with R_f 0.95, M^+ 497.

Korsidinedione. A mixture of 0.3 g of korsidine in 2 ml of acetic acid and 0.15 g of chromium trioxide in 4 ml of 80% acetic acid was heated in the water bath for 30 min and was then evaporated in vacuum, the residue was dissolved in water, the solution was made alkaline with ammonia, and the oxidation product was extracted with chloroform. From the residue after the distillation of the chloroform by treatment with acetone was obtained a diketone – korsidinedione – mp 215-217°C (acetone), R_f 0.87, M^+ 399.

Dihydrokorsidine. Korsidine (0.3 g) was hydrogenated in glacial acetic acid according to Adams (0.25 g of PtO_2). The acetic acid solution after separation from the platinum black was diluted with water, made alkaline with ammonia, and extracted with chloroform. This gave dihydrokorsidine with mp 254-256°C (acetone), R_f 0.70. Mass spectrum: m/e 98, 111 (100%), 112, 124, 125, 138, 139, 150, 162, 164, 178, 179, 344, 345, 359, (M–29), (M–15), 415 M^+.

Diacetyldihydrokorsidine. Dihydrokorsidine (0.05 g) was acetylated with acetic anhydride (1 ml) in pyridine (1 ml) as for the acetylation of korsidine itself. Amorphous diacetyldihydrokorsidine with R_f 0.93, M^+ 499, was obtained.

Dihydrokorsidinedione. Dihydrokorsidine (0.2 g) was oxidized with chromium trioxide (0.1 g) in acetic acid (5 ml) as for the oxidation of korsidine. Yield 0.12 g, mp 226-228°C (acetone), R_f 0.80, M^+ 411.

SUMMARY

1. Sevkorine, korseveriline, severtzidine, and the new alkaloid korsidine have been isolated from the combined alkaloids of the epigeal part of *Korolkovia severtzovii* Rgl.

2. On the basis of a study of the chemical and physical properties of the alkaloid itself and the products of its transformation, and also its conversion into the known alkaloid petilininedione the structure and configuration of korsidine have been established as 3α,6β-dihydroxy-Δ^8-cevanene.

LITERATURE CITED

1. R. N. Nuriddinov and S. Yu. Yunusov, Dokl. Akad. Nauk, UzSSR, No. 5, 47 (1962).
2. K. Samikov, R. Shakirov, D. U. Abdullaeva, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 269 (1976).
3. R. N. Nuriddinov and S. Yu. Yunusov, Khim. Prirodn. Soedin., 258 (1968).
4. K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 367 (1976).
5. R. N. Nuriddinov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 773 (1971).
6. H. Budzikiewicz, Tetrahedron, 20, 2267 (1964).
7. R. N. Nuriddinov, B. Babaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 261 (1968).
8. R. Nuriddinov and S. Yu. Yunusov, Khim. Prirodn. Soedin., 260 (1968).
9. T. M. Moynehan, K. Schofield, R. A. V. Jones, and A. R. Katritzky, J. Chem. Soc., 2637 (1962).
10. R. N. Nuriddinov, A. I. Saidkhodzhaev, M. R. Yagudaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 333 (1968).

11. R. F. Zürcher, Helv. Chim. Acta, 46, 2054 (1963).
12. J. Fried, P. Grabowich, E. F. Sabo, and A. I. Cohen, Tetrahedron, 20, 2297 (1964).

THE STRUCTURE OF REGELINE

D. A. Abdullaeva, M. K. Yusupov, and Kh. A. Aslanov

UDC 547.944.6

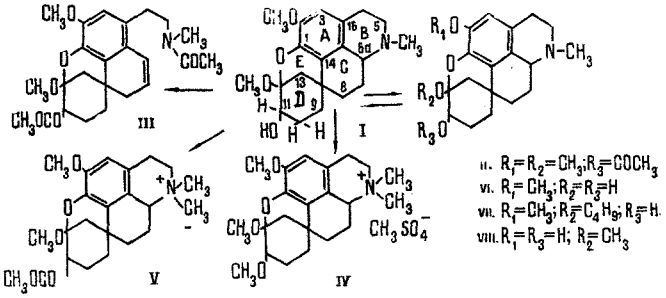
The isolation from the epigeal parts of *Colchicum kesselringii* Rgl. of a new base — regeline — with the composition $C_{20}H_{27}O_4N$, mp 198-200°C, and $[\alpha]_D$ +93° has been reported previously [1]. Its UV spectrum has absorption maxima at 216, 225, and 290 nm (log ε 4.04, 3.96, and 3.37). The IR spectrum of regeline shows absorption bands of a hydroxy group (3200 cm^{-1}), of the C=C bonds of a benzene ring (1600 cm^{-1}), and of methylene groups (1460 cm^{-1}). The mass spectrum of the base has the peaks of ions with m/e 345 (M^+, 65%), 344 $(M-1)^+$ (100%), 330, 326, 302 $(M-43)^+$, 286, 258, 244, 242, 205, 202.

The NMR spectrum of regeline (Fig. 1) shows the signals of a N-methyl group (three-proton singlet at 2.36 ppm), of two O-methyl groups (three-proton singlets at 3.34 and 3.74 ppm) and of a proton in a benzene ring (one-proton singlet at 6.42 ppm).

In the spectral characteristics given, regeline is close to the homoproaporphine and proaporphine bases [2-6]. On the basis of the developed formula, it may be assigned to derivatives of homoproaporphine with a spirocyclohexane ring.

Depending on the conditions, the acetylation of regeline with acetic anhydride led to O-acetyl (II) and O,N-diacetyl (III) derivatives. The formation of the latter shows that the molecule of the base contains a tetrahydroisoquinoline fragment [7], and one of the oxygen atoms is present in the form of a hydroxy group. This hydroxy group possesses an alcoholic nature: it is not methylated by diazomethane nor by methyl iodide in the presence of alkalis. It can be methylated with dimethyl sulfate, which gives N,O-dimethylregeline methosulfate (IV).

The secondary alcohol nature of the hydroxy group of regeline which is probably, by analogy with other alkaloids of this series, located at the C_{11} atom, is confirmed by ready acetylation with acetyl chloride. By acetylating regeline methiodide, we obtained its acetyl derivative (V).



Scheme 1

Regeline is stable to the action of aqueous alkali and ammonia. On being heated with dilute acids, one of its methoxy groups is hydrolyzed with the formation of norregeline (VI). In alcoholic solutions of hydrogen chloride, the base undergoes a transesterification reaction with the formation of the corresponding alkylnorregelines. By heating regeline in n-butanol we isolated O-butylnorregeline (VII). These transformations show that one of the

V. I. Lenin Tashkent State University. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 783-787, November-December, 1976. Original article submitted May 28, 1976.