SUMMARY

The structures of two alkaloids of a new type from the epigeal part of *Nitraria komarovii* have been established. Their synthesis has been performed. The 3-[β-(quinolin-8'-yl)carbonylamino]ethylindole obtained in the course of the synthesis, which has not been described previously in the literature, has been characterized.

LITERATURE CITED

1. T. S. Tulyaganov, A. A. Ibragimov, and S. Yu. Yunusov, Khim. Prir. Soedin., 732 (1980).
2. T. S. Tulyaganov, A. A. Ibragimov, and S. Yu. Yunusova, Khim. Prir. Soedin., 732 (1980).
3. A. A. Ibragimov, S. M. Nasirov, V. T. Andrianov, S. Kh. Maekh, Yu. T. Struchkov, and S. Yu. Yunusov, Khim. Prir. Soedin., 273 (1975).
4. T. S. Tulyaganov, A. A. Ibragimov, and S. Yu. Yunusov, Khim. Prir. Soedin., 737 (1979).
5. K. N. Campbell, J. F. Kerwin, P. A. Lafarge, and B. K. Campbell, J. Am. Chem. Soc., 68, 1844 (1946).
6. F. T. Tyson and T. Shaw, J. Am. Chem. Soc., 74, 2273 (1952).
7. O. Massayuki, K. Masazumi, and M. Sasamoto, J. Pharm . Soc. Jpn., 76, 409 (1956); Chem. Abstr., 50, 13930 (1956).
8. T. Kametani, S. Takano, S. Hibino, and M. Takeshita, Synthesis, No. 9, 475 (1972).
9. T. Kametani, M. Kawara, and K. Fukumoto, Tetrahedron, 30, No. 9, 1053 (1974).
10. É. A. Markaryan, L. P. Solomina, and E. S. Marashayan, Arm. Khim. Zh., 25, No. 8, 683 (1972).

STRUCTURE OF ISOREGELINONE

A. M. Usmanov and M. K. Yusupov

UDC 547.944.6

From a fraction of the bases of *Colchicium kesselringii* Rgl., growing in the Tashkent Province, a new compound which has been called isoregelinone has been isolated. On the basis of spectral characteristics, especially the INDOR spectrum, and chemical transformations, a structure epimeric with that of regelinone has been proposed for it.

Information has been given previously [1-3] about the alkaloids of *Colchicium kesselringii* Rgl. (Kesselring's autumn crocus) growing on the left bank of the middle course of the R. Syrdar'ya. The main alkaloid in it is kesselringine — a phenolic base of the homoproaporphine series [4, 5]. Continuing an investigation of the autumn crocus collected in the Srednechirchikskii region, we have found a comparatively low content of total alkaloids (0.29%) and a qualitatively different composition of the fraction of strong bases. The main part of the total material here also consists of alkali-soluble bases. However, this fraction consists mainly of luteine [6] — an epimer of kesselringine — which we found somewhat unexpected. Luteine, isolated previously from *Colchicum luteum* Baker [7] has not been detected in *C. kesselringii* growing in the Syrdr'ya region.

From the same fraction of bases by chromatography on a column we have isolated a new compound with the composition $C_{19}H_{19}O_5N$, mp 321-323°C which has been called isoregelinone (I). The base possesses no phenolic character. Its passage into the alkaline solution during the separation of the alkaloids of basic nature is due to its relatively better solubility in water than in chloroform.

The IR spectrum of (I) has absorption bands at 3250 and 1690 cm^{-1} showing the presence of hydroxy and carbonyl groups. From the nature of its PMR spectrum (Fig. 1), the base differs from the homoproaporphine compounds that are characteristic for this plant [4, 8, 9] and is similar to regelinone [10]. In the low-field part of the spectrum a one-proton

---

V. I. Lenin Tashkent State University. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 195-199, March-April, 1981. Original article submitted October 2, 1980.

0009-3130/81/1702-0152$07.50

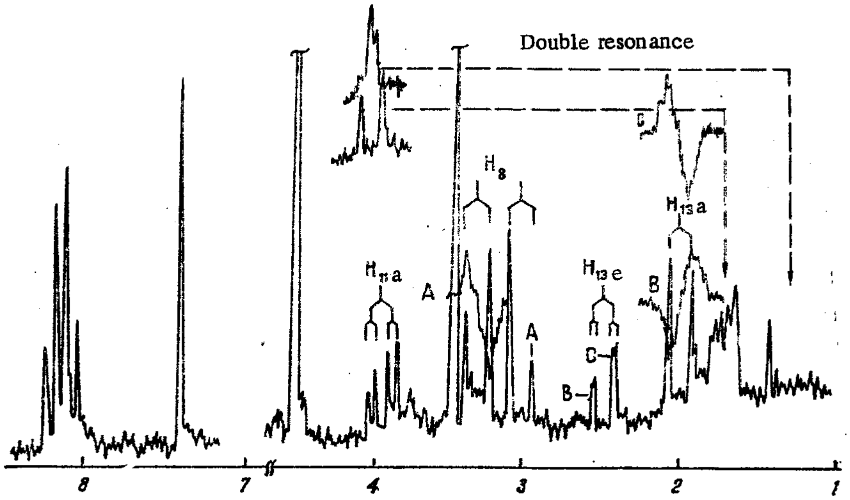


Fig. 1

singlet observed at 7.38 ppm due to a proton of a benzene ring (C_3) and the signals of two protons of the AB type forming doublets with centers at 8.05 and 8.19 ppm with a coupling constant J = 7.0 Hz. The position and nature of the splitting of the signals of these protons correspond to the heterocyclic part of the isoquinoline fragment of the molecule — obviously to the protons at C_4 and C_5. The high-field part of the spectrum of (I) consists of the signals of 15 protons of saturated chains. Of them, 11 form well-resolved signals: Protons of two methoxy groups resonate at 4.36 and 3.34 ppm. One of them, judging from the value of the chemical shift (4.36 ppm) is located in a benzene ring, and the other in the aliphatic part of the molecule.

The signals of a methylene group appear at 3.21 and 2.93 ppm with two doublets and a geminal constant of 13.5 Hz. The downfield shift of its signals is due to the presence of a carbonyl group in the α position to it. In view of the correspondence of the signals of the other protons to the methylene groups of the spirocyclohexanol ring, this methylene group can be assigned position C_7 or C_8. The closeness of the stretching vibrations of the carbonyl group of the base (1690 cm^{-1}) to those of α,β-unsaturated ketones permits it to be assigned to C_7, and the methylene group to the C_8 position. Consequently, isoregelinone belongs to the 7-oxohomoproaphorphine alkaloids.

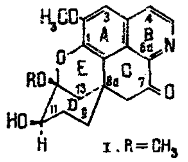
It follows from the facts presented that the hydroxy group is present in the spirocyclane ring of the base. Results obtained previously [6] and the biogenetic closeness of the homoproaporphine alkaloids of the autumn crocus permitted it to be assigned to position C_{11}.

One of the methylene groups of (I), obviously that at C_{13}, manifests itself in the PMR spectrum by the following signals: doublet at 1.91 ppm (H_{13a}) with a coupling constant J = 13.5 Hz, and a doublet of doublets at 2.41 ppm (H_{13e}) with J = 13.5 and 2.0 Hz. The 13.5 Hz constant corresponds to the geminal spin–spin coupling of the H_{13a} and H_{13e} protons, and the 2.0 Hz constant to the long-range interaction of H_{13e} with the equatorial H_{9e} proton [6].

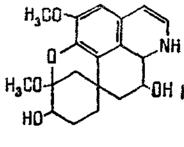
The methylene groups at C_9 and C_{10} form a complex four-proton signal in 0.9-1.8 ppm region. The presence of signals from the protons of C_{10} methylene group in this region is confirmed by the results of double-resonance experiments. The complex form of their splitting because of overlapping with the signals of the C_9 protons leads to an uninterpretable form of the INDOR spectrum of the C_{11} proton for this region. However, it is possible to determine the approximate position of the signals of the protons at C_{10}: The axial proton (H_{10a}) resonates in the 0.9-1.3 ppm region, and the equatorial proton (H_{10e}) in the 1.5-1.8 ppm region. The proton in the C_{11} position forms a well-resolved signal with doublet–doublet splitting at 3.82 ppm. The magnitude of the chemical shift corresponds to its geminal position with respect to the hydroxy group, and the two splitting constants — 11.5 and 5.0 Hz — indicate the presence of only two protons in the α position at C_{10} and the absence of protons in the C_{12} position. The existence of a large spin–spin coupling constant (11.5 Hz) shows the axial arrangement of the C_{11} proton.

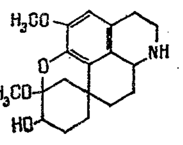
When (I) was heated in dilute acids, hydrolysis took place to give dimethylisoregelinome (II). On methanolysis, this was reconverted into (I). These transformations indicate that the aliphatic methoxy group of the base is present in a cyclic acetal grouping. Its position at C_{12} and its equatorial orientation in ring D, and also the chair form of the latter follow from the results for similar compounds given in the literature [4, 8, 9].

When compound (I) was reduced with zinc dust, compounds (III) and (IV) were isolated, and their structures were confirmed by PMR and mass spectroscopy.

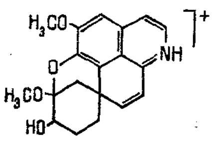

I. R=CH₃

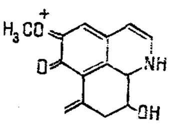
II. R=H

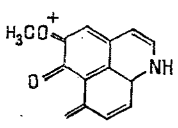

III


IV

The mass spectrum of (I) differs from that of regelinone only by the intensities of the peaks of the individual ions. According to its mass spectrum, compound (IV) is similar to the homoproaporphine bases [11, 12], while (III) differs somewhat from them. Characteristic for compound (III) are fairly strong peaks of ions with m/e 326 and 226 due to the splitting out of a molecule of water from the ions with m/e 344 $(M-1)^+$ and 244 $(M-101)^+$, respectively, which is a confirmation of the presence of a hydroxy group in ring C of the base.


m/e 326


m/e 244


m/e 226

In the PMR spectrum of (II) the signals of two aromatic protons in the ortho position appear, which shows the retention of a double bond in the C_4-C_5 position. Consequently, in this compound reduction has taken place at the double bond at $C_{6a}-N$ and at the carbonyl group — to a secondary alcohol. In compound (IV), the double bonds of ring B and the carbonyl group have been reduced completely.

The facts given above permitted the structure (I), representing an epimer of regelinone, to be suggested for isoregelinone.

EXPERIMENTAL

The composition of the mixture of alkaloids and the individualities of the compounds were studied by thin-layer chromatography in LS 5/40 silica gel containing 13% of gypsum in the chloroform—methanol—acetone—benzene—25% ammonia (10:8:6.5:3.5) system (1) and by paper chromatography in the n-butanol—hydrochloric acid—water (40:7.5:13.5) system (2).

IR spectra were taken on a UR-10 double-beam spectrometer, PMR spectra on an XL-100 instrument, and mass spectra a Varian MAT-311 spectrometer.

Isolation of the Alkaloid Reaction. The epigeal part of the autumn crocus collected in the fruit-bearing period (3.9 kg) was extracted with methanol. The solvent was distilled off and the total extractive substances were treated as described elsewhere [13]. Alkaloid fractions were obtained in the following amounts: neutral substances 1.69 g (0.04%); phenolic-acidic substances 1.88 g (0.05%); alkali-soluble bases 6.27 g (0.16%); and insoluble bases 1.6 g (0.04%).

Isoregelinone (I). The fraction of alkali-soluble bases consisted of five compounds, with R_f 0.33, 0.36, 0.48 (I), 0.76 (luteine), and 0.80 (system 1), and R_f 0.29, 0.49 (I), 0.60 (luteine), 0.78, and 0.86 (system 2). From the sizes of the spots, the main substance in the fraction was luteine, and the compounds with R_f 0.33 and 0.80 were present only as traces.

The mixture of bases (3.09 g) was chromatographed on a column containing 80 g of cellulose in system 2. The fractions of the eluates were monitored by paper chromatography. The substances were isolated from the eluates containing individual compounds by evaporation in vacuum after preliminary neutralization. The bases obtained were purified by passage through a layer of alumina (activity grade II).

This gave 1.02 g of luteine with mp 227-229°C (from acetone), $[\alpha]_D^{22}$ +95° (c 1.45; chloroform), 0.18 g of isoregelinone, and 0.09 g of a base with R_f 0.29, mp 284-286°C (from acetone).

Isoregelinone, mp 321-323°C (from a mixture of acetone and methanol) possesses weakly basic properties. It is readily soluble in methanol and water, less soluble in chloroform and acetone, and insoluble in diethyl ether and petroleum ether.

IR spectrum (cm^{-1}): 3250, 1690.

PMR spectrum (in $CF_3COOH + D_2O$, ppm): 7.78 (1 H, s); 8.05; 8.19, J = 7 Hz (2 H, dd); 4.36 (3 H, s), 3.34 (3 H, s).

Mass spectrum (m/e): 341 (M^+) (100%), 326, 323, 313, 309, 298, 294, 282, 256, 244, 242, 241, 240, 232, 230, 228, 226, 213, 212.

Demethylisoregelinone (II). A solution of 0.05 g of (I) (R_f 0.49) in 10 ml of 5% sulfuric acid was heated for 2 h. After neutralization, the solution was evaporated and the residual substance was purified on alumina (with elution by chloroform and methanol). In this way, 0.03 g of (II) was isolated; R_f 0.17; M^+ 327.

Methylation of (II) to form (I). A solution of 0.02 g of (II) in 7 ml of a 6% solution of hydrogen chloride in methanol was boiled for 1 h. After evaporation of the solvent, the residue was dissolved in water, and the solution was neutralized with ammonia and evaporated. A compound was isolated which was identified by its R_f values in systems 1 and 2 as (I).

Reduction of (I) to (III) and (IV). Zinc dust (a total of 2 g) was gradually added to a solution of 0.1 g of (I) in a mixture of 10 ml of acetic acid and 10 ml of dilute (1:1) hydrochloric acid. After a day, the solution was filtered, made alkaline with ammonia, and extracted with chloroform. After drying and the distillation of the solvent, compound (IV) was isolated with R_f 0.57 (system 1).

PMR spectrum (in $CDCl_3$, ppm): 6.70 (1 H, s), 3.40 (3 H, s), 3.80 (3 H, s).

Mass spectrum (m/e): 331 (M^+), 330 $(M-1)^+$ (100%), 302 $(M-29)^+$, 258, 230, 228, 192.

The aqueous solution after extraction with chloroform was carefully evaporated, and the dry residue was passed through a layer of alumina. Elution with a mixture of chloroform and methanol (8:2) yielded substance (III) with R_f 0.30.

PMR spectrum (in CD_3OD, ppm): 6.92 (1 H, s), 7.47 and 7.90, J = 7 Hz (2 H, dd); 3.44 (3 H, s); 4.10 (3 H, s).

Mass spectrum (m/e): 345 (M^+), 344 $(M-1)^+$ (100%), 326 $(M-19)^+$ 244, 226.

SUMMARY

1. The bases of *Colchicum kesselringii* Rgl., growing in the Srednechirchikskii region have been studied. Two new compounds with mp 321-323°C and 284-286°C have been isolated.

2. According to IR, PMR, and INDOR spectra and the results of chemical transformations, a structure which is that of an epimer of regelinone has been proposed for the first base, with the composition $C_{19}H_{19}O_5N$, and it has been called isoregelinone.

LITERATURE CITED

1. M. K. Yusupov and A. S. Sadykov, Zh. Obshch. Khim., 34, 1672 (1964).
2. M. K. Yusupov, in: The Chemistry of Plant Substances [in Russian], Tashkent (1972), p. 19.
3. M. K. Yusupov and A. S. Sadykov, Uzb. Khim. Zh., No. 5, 49 (1961).
4. M. K. Yusupov and A. S. Sadykov, Khim. Prir. Soedin., 350 (1976).
5. M. K. Yusupov, N. L. Mukhamedyarova, A. S. Sadykov, L. Dolejs, P. Sědmera, and F. Santavy, Collect. Czech. Chem. Commun., 42, 1581 (1977).
6. N. L. Mukhamed'Y rova, M. K. Yusupov, M. G. Levkovich, and Kh. A. Aslanov, Khim. Prir. Soedin., 801 (1976).
7. M. K. Yusupov and A. S. Sadykov, Scientific Proceedings of the V. I. Lenin Tashkent State University. Natural Sciences [in Russian], Tashkent, No. 203 (1962), p. 3.

8. M. K. Yusupov, D. A. Abdullaeva, Kh. A. Aslanov, and A. S. Sadykov, Khim. Prir. Soedin., 383 (1975).
9. D. A. Abdullaeva, M. K. Yusupov, and Kh. A. Aslanov, Khim. Prir. Soedin., 783 (1976).
10. M. K. Yusupov, A. M. Usmanov, A. K. Kasimov, and Kh. Turdikulov, Khim. Prir. Soedin., 867 (1977).
11. A. K. Kasimov, M. K. Yusupov, E. Kh. Timbekov, and Kh. A. Aslanov, Khim. Prir. Soedin., 194 (1975).
12. E. Kh. Timbekov, A. K. Kasimov, D. A. Abdullaeva, M. K. Yusupov, and Kh. A. Aslanov, Khim. Prir. Soedin., 328 (1976).
13. M. K. Yusupov and A. S. Sadykov, Scientific Proceedings of the V. I. Lenin Tashkent State University. Collection: The Chemistry of Plant Substances [in Russian], Tashkent, No. 286, Vol. II (1966), p. 56.

ALKALOIDS OF *Delphinium tamarae*

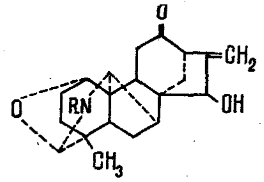
L. V. Beshitaishvili, M. N. Sultankhodzhaev,
K. S. Mudzhiri, and M. S. Yunusov

UDC 547.944/945

The roots of *Delphinium tamarae* Kem. Nath., collected in the period of the withering of the epigeal part of the environs of the village Bakuriani (Georgian SSR) have yielded 2.02% of combined alkaloids. When the combined material was separated, methyllycaconitine, lycoctonine, and anthranoyllycoctonine were isolated, together with a new base having mp 286°C which has been called norsongoramine. The structure of norsongoramine has been shown on the basis of its spectral characteristics and conversion to songoramine.

We have investigated the roots of *Delphinium tamarae* Kem. Nath., collected in the period of the withering of the epigeal part in the environs of the village of Bakuriani, Georgian SSR. The combined alkaloids amounted to 2.02% of the weight of the dry plant. When the combined alkaloids were separated, methyllycaconitine, lycoctonine, anthranoyllycoctonine, and a new base with the composition $C_{20}H_{25}NO_3$, mp 286°C (acetone), were isolated. The NMR spectrum of the new alkaloid contains the signals of tertiary C-methyl group (three-proton singlet at 1.12 ppm) and of a terminal methylene group (broadened one-proton singlets at 4.63 and 4.85 ppm). In the IR spectrum there are the absorption bands of hydroxy groups at 3450 and 3530 cm^{-1} and of a carbonyl in a 6-membered ring at 1710 cm^{-1}.

The mass spectrum of the compound is characteristic for the alkaloids of the songorine group and is similar to that songoramine [1]. In addition to the peak of the molecular ion (M^+ 327), there is a peak of the $M^+ - 56$ ion, showing the presence of the grouping of an internal ether of an α-carbinolamine [1].



I. R=H
II. R=C_2H_5

The difference in the molecular weights of the alkaloid and of songoramine of 28 amu, the absence of the signal of N-ethyl group from the NMR spectrum, and the presence of an internal α-carbinolamine ether grouping have permitted the assumption that the alkaloid is

---

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 199-201, March-April, 1981. Original article submitted November 26, 1980.

0009-3130/81/1702-0156$07.50