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STRUCTURE OF SIBIRINE

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The new optically based sibirine with $[\alpha]_D$ −22.5° (c 0.81; chloroform), M^+ 183, has been isolated from the epigeal part of the *Nitraria sibirica* by column chromatography. On the basis of the results of chemical transformations (acetylation, oxidation), analysis of spectral characteristics (UV, IR, mass, PMR, ORD), and also a comparison of the alkaloid with the N-methyl derivatives of nitramine and isonitramine, the structure of sibirine has been established as methyl-2-azaspiro[5.5]undecan-7-ol.

Continuing an investigation of the total alkaloids of the epigeal part of *Nitraria sibirica* Pall. (family *Zygophyllaceae*) collected in the environs of the village of Rybach'e, KirgSSR, in May 1976 [1], we have isolated a new optically active liquid base with the composition $C_{11}H_{21}NO$, $[\alpha]_D$ −22.5° (c 0.81; chloroform), which we have called sibirine (I), and have obtained a number of derivatives.

In the UV, compound (I) is transparent. The IR spectrum contains an absorption band of active hydrogen at 3320 cm^{-1}. The acetylation of (I) with acetic anhydride led to the O-acetyl derivative of sibirine (II). In the IR spectrum of (II) the absorption band of active hydrogen had disappeared and a strong absorption band of an ester carbonyl group had appeared.

The mass spectrum of (I) contains the peaks of ions with m/z 183 M^+ (100%), 182, 169, 168, 166, 155, 140, 122, 112, 110, 98, 96, 84, 57. Such fragmentation is characteristic for nitramine [2] and isonitramine [1], but it differs from them by 14 m/z.

Since the PMR spectrum of (I) contains a signal from N-methyl protons (2.19 ppm), we assumed that base (I) was the N-methyl derivative of nitramine or of isonitramine. To confirm this, we obtained N-methylnitramine (III) and N-methylisonitramine (IV). The spectral characteristics of compound (IV) (IR, PMR) were identical with those of sibirine. The IR spectra of the O-acetyl derivatives of (I) and (IV) are also identical.

In the PMR spectrum of (I) at 3.54 ppm there is a well-defined one-proton multiplet with a half-width of the line of 18 Hz, which is apparently due to the proton at C_7 geminal to the hydroxy group. The half-width of the signals shows the axial orientation of this proton and, consequently, as in isonitramine [1], the equatorial nature of the hydroxy group.

The ORD curves of (I) and (IV) are similar in nature but opposite in sign. The signs of the optical rotations of these bases are also opposite.

Thus, it follows from the facts given above that sibirine is the antipode of N-methylisonitramine and has the structure of 2-methyl-2-azaspiro[5.5]undecan-7-ol (I).

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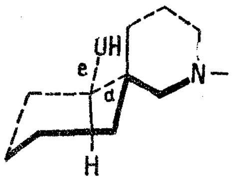

I

EXPERIMENTAL

The UV spectrum was taken on a Hitachi spectrometer (in ethanol); IR spectra on a UR-20 instrument (in the form of a film and with KBr): mass spectra on a MKh-1303 spectrometer fitted with a system for direct introduction into the ion source; PMR spectra on a JNM-4H-100/100 Hz instrument (HMDS, δ scale); and ORD spectra on a JASCO J-20 spectropolarimeter in chloroform.

The homogeneity of the substances was checked by chromatography in a thin layer of KSK silica gel in the following solvent systems: 1) benzene—methanol (4:1); 2) chloroform—methanol (1:1); 3) chloroform—methanol—ammonia (1:1:0.1).

The revealing agents were: a) Dragendorff's reagent, and b) iodine vapor.

Isolation of Sibirene (I). The pH 6 fraction obtained after the citrate-phosphate buffer separation of the ether-extracted total material from the epigeal part of *Nitraria sibirica* [1] (2.64 g) was chromatographed on a column of silica gel. Elution was performed with chloroform and then with chloroform—methanol (95:5); similar fractions were combined and were separated preparatively on plates with a fixed layer (silica gel—glysum). This gave pure sibirine in the form of an oil (0.3 g). PMR (ppm); 4.94 (O-H); 3.54 (7_a-H); 2.73 (3_e-H); 2.52 (1_e-H); 2.19 ($N-CH_3$). IR (cm^{-1}): 3320, 2935, 2860, 2790, 1455; the last-mentioned bands were the weakest.

Sibirine Hydrochloride. An alcoholic solution of HVl was added dropwise to an acid solution of the base until the reaction was weakly acidic. The crystalline salts that had deposited were separated off and recrystallized from acetone—ethanol; mp 191-192°C.

O-Acetylsibirine (II). A solution of 0.057 g of the base in 3.5 ml of acetic anhydride was treated with 0.09 g of p-toluenesulfonic acid and the mixture was heated at 100°C for 2 h. Then it was cooled with ice and was made alkaline with sodium carbonate, and the substance was extracted with ether. After the solvent had been distilled off, 0.54 g of the oily compound (II) was obtained, IR: 1735 cm^{-1} $(\text{—O—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—})$; M^+ 225.

7-Oxosibirine. A mixture of 0.164 g of sibirine, 0.03 g of chromium trioxide, and 0.8 ml of acetic acid was left at room temperature for three days. Then the solvent was driven off in vacuum, the dry residue was treated with 2 ml of water, and the mixture was made alkaline with 5% NaOH solution. The reaction product was extracted with ether. This gave 0.010 g of an oily ketone. IR: 1710 cm^{-1} $(\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—})$.

M-Methylnitramine (III). This was obtained by the reaction of the base with methyl iodine [1]. M^+ 183; $[\alpha]_D$ +17° (c 0.43, chloroform); PMR (ppm): 5.43 (O-H); 3.42 (7_a-H); 3.07 (1_e-H); 2.67 (3_e-H); 2.16 ($N-CH_3$) [1]. IR (cm^{-1}): 3290, 2935, 2860, 2800, 1445, 1070; the last-mentioned bands were the weakest.

N-Methylisonitramine (IV). This was obtained in a similar manner to (III). M^+ 183; $[\alpha]_D$ +25° (c 0.48; chloroform); PMR (ppm); 5.39 (O-H); 3.54 (7_a-H); 2.73 (3_e-H); 2.51 (1_e-H); 2.17 ($N-CH_3$) [1]. IR (cm^{-1}): 3320, 2935, 2860, 2790, 1455; the last-mentioned bands were the weakest.

CONCLUSION

For the new alkaloid from the epigeal part of *Nitraria sibirica*, sibirine, the structure of 2-methyl-2-azaspiro[5.5]undecan-7-ol has been established.

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BAICALINE — A NEW APORPHINE ALKALOID FROM *Thalictrum baicalense*

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A new aporphine base — baicaline — has been isolated from the epigeal part of *Thalictrum baicalense*. Its structure has been established as 1,9,10-trimethoxy-2,3-methylenedioxynoraporphine. Magnoflorine and berberine have been isolated from the roots of the plant.

Continuing a study of Far Eastern species of *Thalictrum*, we have investigated the peculiar East Asian species *Th. baicalense* Turcz. [Baikal meadow-rue], which, according to "Flora SSSR" ["Flora of the USSR"] belongs to the section *Physocarpum* DC [1], but which is well distinguished from other meadow-rues by its swollen ovate-spherical woody fruit. On the basis of features of the structure of the generative organs, M. Emura [2] isolated this species into a monotypical section *Baicalensia* (Tamura) Eruma. The Baikal meadow-rue is distributed in the southern part of Eastern Siberia in the Soviet Far East in the basin of the R. Amur, and on the Karelian peninsular, where it grows among valley woods and on their outskirts in thickets.

For the investigation we took the roots and epigeal part of *Th. baicalense* Turcz., collected on June 20, 1976 in the environs of the village of Kuldur, Khabarov district. The methanolic extraction of the roots yielded 0.7% of combined bases, from which magnoflorine and berberine were extracted. The epigeal part was extracted with chloroform. From the mixture of alkaloids (0.50% on the weight of the raw material), a crystalline optically active base (I) was isolated. UV spectrum of (I), $\lambda_{\max}^{\text{ethanol}}$, nm: 220, 246, 287, 303, 315.

The PMR spectrum of (I) contained the signals of the protons of three methoxy groups (nine-proton singlet at 3.91 ppm), of a methylenedioxy group (broadened two-proton singlet at 6.03 ppm), and of two aromatic protons at 6.82 and 7.94 ppm (singlets, one proton each). The mass spectrum contained the peaks of ions with m/z 355 (M^+) 354. 340, and 326 $(M - 29)^+$. The combination of UV, NMR, and mass-spectroscopic characteristics showed that (I) was a new pentasubstituted noraphorphine base. We have called it baicaline. The noraporphine nature of (I) was confirmed by the preparation of N-methyl- and N-acetylbaicalines (II and III).

In the study of the structure of baicaline, the largest amount of information was provided by NMR spectra. One-proton singlets at 6.82; 7.94; 6.70, 7.80; 6.63, 7.75 ppm in the spectra of (I), (II), and (III) are due to the H-8 and H-11 protons, respectively [3]. Consequently, baicaline is a 1,2,3,9,10-pentasubstituted aporphine base in which the methylenedioxy group may be present at C-1,2; C-2,3; or C-9,10. A methylenedioxy group at C-1,2 appears in the form of two one-proton doublets at about 6.0 and 5.75 ppm (J ≈ 1.5 Hz), and one in the 9,10 position is revealed in the form of a two-proton singlet at ≅6.0 ppm [4]. In the case of 2,3-substitution (ocokryptine (IV) and O-methylocokryptine (V)) close one-proton doublets are observed at 5.98, 5.92 and 5.91, 5.88 ppm [5]. In the structure of (II) and (III), the protons of the CH_2O_2 group appear in the form of two broadened singlets at 5.91, 5.89 and 5.83, 5.86, respectively. On the basis of what has been said above, the 2,3 position is suggested for the methylenedioxy group in baicaline. Furthermore, 3,9,10-trimethoxy-1,2-methylenedioxynoraporphine (northalicmine (VI) [6]) is not identical (melting point, IR and NMR spectra) with baicaline, nor is N-acetyl-1,3,4-trimethoxy-9,10-methylene-

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