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ALKALOIDS OF *Arundo donax*. XIV. CRYSTAL AND MOLECULAR STRUCTURE OF N-METHYL-TETRAHYDRO-*β*-CARBOLINE

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*An indole alkaloid of the N-methyl-tetrahydro-*β*-carboline series was isolated for the first time from* Arundo donax, *Poaceae. Its structure was solved by X-ray structure analysis.*

Key words: *Arundo donax*, Poaceae, N-methyl-tetrahydro-*β*-carboline, X-ray structure analysis.

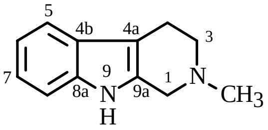
In continuation of the separation of the total alkaloids from roots of *Arundo donax* L. (Poaceae, grasses) [1] collected during the early vegetative period in Fergan district, we chromatographed the total $CHCl_3$ bases over columns of Al_2O_3. Rechromatography of individual fractions isolated an alkaloid with mp 216-218°C (**1**).

The UV spectrum of **1** contains maxima at 224 and 280 nm (log ε 3.50 and 3.90, respectively). The IR spectrum has absorption bands for active H (3130 cm^{-1}) and an aromatic ring (1622, 870 cm^{-1}). The mass spectrum gives a peak for the molecular ion with *m/z* 186 and peaks for ions with *m/z* 143 and 116, which are characteristic of an indole ring [2].

The PMR spectrum of **1** in $CDCl_3$ exhibits a 3H singlet at 2.40 ppm for protons of an NCH_3 group, a 2H singlet at 3.46 ppm for C-1 methylene protons, and a 4H singlet at 2.42 ppm for the C-3 and C-4 methylene protons. The 4H singlet at 2.42 ppm splits into two 2H doublets centered at 2.62 and 2.76 ppm in the PMR taken in pyridine. The signal for the C-1 methylene undergoes a paramagnetic shift by 0.10 ppm and is observed at 3.56 ppm. Signals for four aromatic protons appear in the range 6.90-7.60 ppm.

These spectral properties indicate that **1** is a *β*-carboline alkaloid.

The structure of **1** was proved by an X-ray structure analysis (XSA). It was demonstrated that the isolated compound is indeed an indole alkaloid with the structure N-methyl-tetrahydro-*β*-carboline [3, 4]:



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It is interesting to note that the observation of this alkaloid in the roots of *Arundo donax* is the first instance of the isolation of an alkaloid of this type from a representative of the cereals.

Figure 1 shows the molecular structure of **1** according to the XSA. It can be seen that the tricyclic pseudoaromatic indole core, including C1 and C4, is planar within ±0.017 Å. The third six-membered ring has the half-chair conformation with N2 and C3 deviating to opposite sides of the aforementioned plane (by 0.52 and 0.20 Å, respectively), although this ring in well-known 1,2,3,4-tetrahydro-2-carboline adopts the two statistical shapes of a half-chair and distorted boat with probabilities of 0.80 and 0.20, respectively [5]. The bond lengths and angles in **1** are in general close to those observed in related indole alkaloids [1, 5].

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TABLE 1. Atomic Coordinates (×10^4) and Equivalent Thermal Parameters U_{eq} ($Å^2$×10^3) in molecule **1**

Atom	x	y	z	U_{eq}
C1	1228(3)	-1456(6)	7297(3)	46(1)
N2	815(2)	328(5)	7779(2)	44(1)
C3	21(4)	1598(7)	6957(3)	56(1)
C4	548(4)	2673(7)	6209(4)	57(1)
C4a	1343(3)	1213(6)	5921(3)	44(1)
C4b	1948(3)	1402(6)	5171(3)	46(1)
C5	1999(4)	2934(7)	4417(3)	58(1)
C6	2677(4)	2580(9)	3799(4)	68(1)
C7	3309(4)	748(9)	3913(4)	68(1)
C8	3292(4)	-779(8)	4651(4)	60(1)
C8a	2605(3)	-438(6)	5280(3)	46(1)
N9	2410(3)	-1687(5)	6053(3)	49(1)
C9a	1652(3)	-651(6)	6441(3)	41(1)
C10	273(4)	-496(9)	8531(4)	60(1)

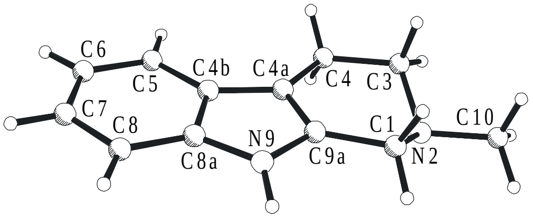

Fig. 1. Molecular structure of N-methyl-tetrahydro-*β*-carboline.

Atom N2 has a tetrahedral configuration. The methyl group on it is situated equatorially. The unshared electron's pair of atom N2 is axial and participates in intermolecular H-bonds in the crystal. H-bonds N9–H...N2 are formed with the following parameters: N2...N9, 2.99 Å; N2...H, 2.07 Å; N9–H...N2, 166°. As a result, an infinite chain is formed along the *n* glide plane.

EXPERIMENTAL

IR spectra were recorded on a Perkin—Elmer Model 2000 Fourier spectrometer in KBr disks; mass spectra, in an MX 1310 spectrometer with direct sample introduction into the ion chamber. PMR spectra were recorded on a Tesla BS-567 A/100 MHz instrument ($CDCl_3$ solvent, 0 = HMDS, σ-scale).

TLC used Al_2O_3 with elution by ether (1), benzene (2), and $CHCl_3$:CH_3OH (19:1) (3).

Isolation of N-Methyl-tetrahydro-*β*-carboline. The total $CHCl_3$ alkaloids (19 g) of *A. donax* were chromatographed over an Al_2O_3 column (Brockman, activity II, 1:20) with elution by $CHCl_3$ (fractions of 150 mL volume). Fractions 1-2 (0.85 g) were rechromatographed over an Al_2O_3 column (1:30) with elution by hexane:ether (7:1) and benzene (fractions of 8 mL volume). Benzene fractions 7-15 were worked up with acetone to isolate **1** (25 mg), mp 216-218°C (benzene), R_f 0.26 (system 1), 0.43 (system 2), 0.45 (system 3).

X-ray Structure Analysis. Crystals of composition $C_{12}H_{14}N_2$ (**1**) were obtained from ethanol solution. A transparent single crystal at 293 K was used for the XSA. Crystals of **1** are monoclinic: a = 12.700(3), b = 6.308(1), c = 13.246(3) Å, β = 107.57(3)°, V = 1011.7(4) $Å^3$, d_{calc} = 1.223 g/cm^3, absorption coefficient μ = 0.074 cm^{-1}, space group $P2_1/n$, Z = 4. Intensities of 1991 independent reflections were measured on a Stoe Stadi-4 automated diffractometer (Mo Kα-radiation, graphite monochromator, ω/2θ-scanning, $2\theta_{max}$ = 50°). Absorption corrections were not applied.

The structure was solved by direct methods using the SHELXS-86 program set. Nonhydrogen atoms were refined (SHELXS-93) anisotropically using full-matrix least-squares methods (on F^2). Positions of H atoms were found in a difference Fourier synthesis and refined with fixed isotropic thermal parameters $U_{iso} = nU_{eq}$, where $n = 1.5$ for methyls and 1.2 for others and U_{eq} is the equivalent isotropic thermal parameter of the C and N atoms. The final agreement factors were $R_1(F) = 0.0952$, $wR_2(F^2) = 0.3209$, and GOF = 0.95 for independent reflections [$R_1(F) = 0.0618$ and $wR_2(F^2) = 0.1995$ for 1383 reflections with $I > 2\sigma(I)$] included in the final refinement cycles. Table 1 lists coordinates of nonhydrogen atoms from the final least-squares cycle.

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